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Potential Nano-Enabled Environmental Applications for Radionuclides

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Potential Nano-Enabled Environmental Applications for Radionuclides

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Preface

"Potential Nano-Enabled Environmental Applications for Radionuclides" is an informational document designed to familiarize interested parties with some of the emerging nanotechnologies, and to recognize their potential environmental applications and implications. Specifically, it is developed to assist in decision making for incorporating nano-enabled technologies in mitigation of environmental contaminants including radionuclides. The document represents a snapshot in time to elucidate some of the base knowledge of nano-science which has evolved over the last 5-10 years. For the purposes of this document, "nano-enabled technologies and/or processes" refer to technologies which are enabled by a nano subsystem.

This document may be updated in the future, and if you have any comments on the document or suggestions for incorporation in future updates, please contact: Ms Madeleine Nawar, USEPA, ORIA, RPD, 1200 Pennsylvania Ave., NW (MC 6608J), Washington DC 20460-0001, USA, Phone: 202-343-9229, Fax: 202-343-2306, Email: nawar.madeleine@epa.gov

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Executive Summary

The remediation of radionuclides and heavy metals using current technology is generally a costly and challenging proposition. Though funds for new technology development are limited, the need for innovative technologies and transformational approaches continues to be strong. In recent years, nanotechnology has risen to the forefront and the new properties and enhanced reactivities offered by nanomaterials may offer a new, low-cost paradigm to solving complex environmental and engineering problems. Many U.S. federal agencies, including the U.S. Environmental Protection Agency (EPA), are strongly supporting a wide range of nanotechnology research. Similarly, other countries are also promoting research in this new field.

Environmental technologies frequently emerge as an offshoot of other technological developments or scientific advances. They can also be further enabled by changes in regulatory approach or stakeholder acceptance. Technologies such as real-time contaminant measurements within the EPA Triad framework, bioremediation, permeable reactive barriers, in-situ chemical oxidation, and enhanced attenuation have all been added to the toolbox of environmental technologies over the past decade. During roughly the same period, nanotechnology has evolved from an interesting (albeit arcane) area of manufacturing science, to being heralded as a paradigm-shifting technological revolution in the mold comparable to that of information technology or biotechnology. Coupled with this broad evolution, there has been a considerable amount of interest in nanotechnologies for a wide variety of applications in environmental remediation and waste reduction. For example, zero-valent iron (ZVI) nanoparticles for the remediation of chlorinated organics have effectively become a commercially-available technology. A number of other technologies, such as nano-scale photocatalysts and improved nanofiltration membranes, are also nearing commercialization.

Nanotechnologies applied to the remediation of radionuclides have been a slower area to develop; this may well have been predictable since experience shows that the pathway for development of radionuclide remediation technologies is generally burdened with difficulties. However, it is important to realize that—although our conceptual awareness of nanotechnology is relatively new—nanotechnologies have in fact been used safely and effectively in the management of radioactive waste almost from the start of the nuclear age; zeolites, now recognized as a nanotechnology due to their nanostructure, have been used as ion exchangers to remove radioactive components from aqueous waste solutions for half a century.

In this report, the current, early stages of development of nanotechnology applications for remediation of radionuclides and heavy metals are divided into two areas: new remediation methods and advancements in sensors. Though developments in these fields still remain in their early stages, this report describes some of the more promising remediation nanotechnologies and new sensors, and attempts to extrapolate general developments in nanotechnologies to advances in radionuclide remediation and monitoring. Some emerging examples already exist in both radionuclide remediation and monitoring. For example, the “Lab-on-a-Chip” (LOC) device for analyzing solutions

containing radionuclides and heavy metals is a promising development. Though a recently-emerged technology, the LOC device is being actively investigated in the United States and overseas for modification to radionuclide sensing, is advancing quickly, and is already being applied to radionuclides and heavy metals. Examples of other new sensor advances are reviewed and presented in this report.

There is considerable potential for nanotechnology to assist with the remediation of radionuclide-contaminated sites. For example, ZVI nanoparticles, a reducing agent already implemented for the remediation of chlorinated organics in groundwater, are an excellent prospect for use as a reducing agent to precipitate uranium from contaminated groundwater. ZVI nanoparticles are commercially available, and field tests for remediation of heavy metals such as chromium (IV) have shown promise. Two advantages of ZVI are the greater aerial distribution in saturated porous media and a high degree of reactivity due to the greater surface area of these very fine particles. Another example is the Self Assembled Monolayers on Mesoporous Supports (SAMMS) technology, originally developed by the Department of Energy (DOE) primarily for mercury but also with radionuclides in mind, which has recently had its first field implementation.

There are strong scientific basis and solid research demonstrating that nanotechnologies will make significant advances over a wide range of technological fields. Government agencies around the world and the commercial sector now invest billions of dollars into nanoscience and technology research and development. However, the amount of funding environmental nanoscience research and development receives represents only a fraction of this massive overall effort. Hence, environmental nanoscience has lagged significantly behind other application and development areas in the nanoscience field. Because of growing national and international interest in the environment, it is expected that environmental nanoscience will grow.

This report presents a general introduction to nanotechnology, providing a broad context to its narrower focus on nanotechnology for environmental remediation and waste management. The introduction also addresses some risk considerations involving nanotechnology, and discusses nanotechnology as applied to both environmental remediation (in general) and the environmental remediation of radionuclides (in particular). The body of the document consists of two main sections, one surveying nanotechnologies for remediation, the other surveying nanotechnologies for sensors. These two sections are divided into chapters which describe a nanotechnology or group of related nanotechnologies, and include a brief summary of the environmental potential of each.

1.0 Introduction

1.1 Definition of Nanotechnology

Nanotechnology is the art and science of manipulating matter at the atomic or molecular scale and holds the promise of providing significant improvements in technologies for protecting the environment. While many definitions for nanotechnology exist, the U.S. Environmental Protection Agency (EPA) uses the definition developed by the National Nanotechnology Initiative (NNI), a U.S. Government research and development (R&D) program established to coordinate multi-agency efforts in nanoscale science, engineering, and technology. The NNI is comprised of 26 federal agencies, 13 of which have R&D budgets in nanotechnology. The NNI (NNI 2007) requires nanotechnology to involve all of the following:

1. Research and technology development at the atomic, molecular, or macromolecular levels, in the length scale of approximately 1-100 nanometer (nm) range in any direction;
2. Creating and using structures, devices, and systems that have novel properties and functions as a result of their small and/or intermediate size; and
3. Ability to control or manipulate on the atomic scale.

Nanotechnology is thus the technology of the extremely small; one nm is defined as one billionth of a meter. In comparison, 1 nm is one fifty-thousandth of the diameter of a human hair, or, if a nanometer was scaled to the diameter of a child's marble, then a meter would have to be scaled to the diameter of the Earth. Nanotechnology is often regarded as being a product of the latter part of the twentieth century, a product of the drive towards miniaturization led by the semiconductor industry. However, in a broader sense, nanotechnology has been around, albeit unrealized as such, for a long time. Two thousand years ago the ancient Greeks used a permanent hair-dying recipe that worked by depositing 5 nm lead sulfide crystals inside hair. High-quality steel made in India before the turn of the first millennium has been shown to contain—and owe its outstanding properties to—carbide structures similar to modern carbon nanotubes. Medieval artists colored stained glass using metal nanoparticles. The difference between these ancient examples of "nanotechnology" and the current situation is the ability to understand—or at least embark on a path towards understanding—the fundamental principles underlying nanotechnological behavior, the ability to assess the current state of knowledge, and the ability to systematically plan for the future based on that knowledge.

1.2 Purpose of This Report

The purpose of this report is to assist EPA in its exploration of the potential for using nano-enabled technologies in the cleanup of radioactive contamination, and in decisions to assist with the development of viable technologies in this area. For the purposes of this report, "nano-enabled technologies" refers to technologies that are enabled by a nano sub-system. This report will be used to identify and evaluate emerging applications and

implications (both health and ecological) of nano-enabled technologies for the remediation of sites contaminated with radionuclides.

1.3 Background of Nanotechnology

The history of nanotechnology is generally understood to have begun in December 1959 when physicist Richard Feynman gave a speech, "There's Plenty of Room at the Bottom" (Feynman 1959), at an American Physical Society meeting at the California Institute of Technology in which he identified the potential of nanotechnology. Feynman said it should be possible to build machines small enough to manufacture objects with atomic precision, and that if information could be written on an atomic scale, "all of the information that man has carefully accumulated in all the books in the world can be written ... in a cube of material one two-hundredths of an inch wide—about the size of the smallest piece of dust visible to the human eye." He claimed that there were no physical laws preventing such achievements, while noting that physical properties would change in importance (e.g., gravity becoming less important), though surface phenomena would begin to dominate behavior.

In 1974, Norio Taniguchi first used the word "nanotechnology" (Taniguchi 1974), in regard to an ion sputter machine, to refer to "production technology to get the extra-high accuracy and ultra-fine dimensions, i.e. the preciseness and fineness on the order of one nanometer." In the 1980s, Eric Drexler authored the landmark book on nanotechnology, "Engines of Creation" (Drexler 1986), in which the concept of molecular manufacturing was introduced to the public at large. It is due to Drexler that much of the public's imagination has been captured by the potential of nanotechnology and nanomanufacturing. In 1985, fullerenes, or "buckyballs," were discovered (Kroto et al. 1985). By the 1990s, nanotechnology was advancing rapidly. In 1990, the first academic nanotechnology journal was published, in 1993 the first Feynman Prize was awarded, and by 2000 President Bill Clinton announced the U.S. National Nanotechnology Initiative (NNI). NNI and other nanotechnology proponents now anticipate the development of nano-enabled tools to help address many current challenges facing the United States and the international community, including:

- Clean, secure, affordable energy;
- Stronger, lighter, more durable materials;
- Low-cost filters to provide clean drinking water;
- Medical devices and drugs to detect and treat diseases more effectively with fewer side effects;
- Lighting that uses a fraction of the energy associated with conventional systems;
- Sensors to detect and identify harmful chemical and biological agents; and
- Techniques to clean up harmful chemicals in the environment.

This document focuses on the last of these challenges—techniques to clean up harmful chemicals in the environmental. Nanotechnologies offer new and previously unanticipated possibilities due to new properties and behaviors that occur at the nano scale, which can be harnessed in a structured and planned manner. The growing ability to

design and tailor technologies to specific ends indicates that problems that were once regarded as impossible to solve can now be addressed in a rational manner. The size of nanoparticles allows nanoscale behavior to be introduced into areas inaccessible to conventional technologies. When material exists in the nanoparticulate form, it exhibits unusual behavior that has made it the subject of great interest. This unusual behavior is the result of two phenomena. First, the surface area-to-volume ratio of nanoparticles is much greater than that of larger particles. Nanoparticles in the 10 nm range can have 50% of their molecular structure exposed to the surface, a percentage that is millions of times greater than that of typical powdered materials. Since chemical reactivity and catalytic ability is directly related to surface area, chemical properties are greatly enhanced. Second, at the nanoparticle scale, quantum behavior that is typically masked in larger particles can be readily displayed.

1.4 Application of Nanotechnology

Descriptions of nanotechnology that characterize it purely in terms of the minute size of the physical features with which it is concerned—assemblies between the size of an atom and about 100 molecular diameters—make it sound as though nanotechnology is merely using infinitely smaller parts than conventional engineering. However, working matters are truly more complex; rearranging the atoms and molecules leads to new properties and unusual behaviors. A transition is apparent between the fixed behavior of individual atoms and molecules and the adjustable behavior of collectives. Many scientists are now investigating the fundamental nature of nanotechnology in a wide spectrum of academic fields—from the basic sciences to engineering. Much of known science (e.g., colloid science, electronics, chemistry, physics, and genetics) will be applicable, but augmented with exciting new breakthroughs.

The potential applications of nanotechnology range across a broad scale. For example, in medical systems, it could be possible to improve the tissue compatibility of implants to create scaffolds for tissue regeneration, or perhaps even to build artificial organs. Further, new types of genetic therapies and anti-aging treatments could be possible.

Nanotechnology is currently used by leading businesses and industrial research companies for a variety of technical and innovative applications. Examples include:

- ExxonMobil is using zeolites, minerals with pore sizes of less than 1 nm, as a more efficient catalyst to break down or crack large hydrocarbon molecules to form gasoline.
- IBM has added nanoscale layering to disk drives, thus exploiting the giant magnetoresistive effect to attain highly dense data storage.
- Gilead Sciences is using nanotechnology in the form of lipid spheres, also known as liposomes, which measure about 100 nm in diameter, to encase an anticancer drug to treat the AIDS-related Kaposi's sarcoma.
- Carbon Nanotechnologies, a company co-founded by buckyball discoverer Richard E. Smalley, is making carbon nanotubes more affordable by using a new and more efficient manufacturing process.

- Nanophase Technologies is utilizing nanocrystalline particles, incorporated into other materials, to produce tough ceramics, transparent sun blocks, and catalysts for environmental uses, among other applications.

Though vastly different in the outputs they produce, these companies all use nanotechnology to develop more efficient, affordable, and, most recently, environmentally-safe products.

1.5 Risk Associated with Nanoparticles in the Environment

As previously noted, the potential widespread application of nanomaterials in environmental remediation is made possible by the miniaturization of materials down to the nano-scale. However, this same enabling characteristic also influences risk by changing the particles' potential for mobility, exposure, absorption, reactivity, and toxicity. When a nanomaterial is used for environmental remediation, it is intentionally introduced into the environment to exploit its unique properties. For example, nano-sized colloidal iron nanoparticles can act as catalysts in redox reactions. Of particular concern is the potential mobility of nanoparticles out of targeted sites or tissues, or whether intentional or unintentional releases of highly mobile nano-particles into the environment could be controlled (CRS 2008).

Nevertheless, nanomaterials can have side effects, and a risk assessment requires knowledge of their distribution in the environment and food chain. Risk assessment is required for understanding the nanoparticles' behavior to evaluate potential risks associated with nanomaterial use for remediation. Side effects associated with the use of nanotechnology, especially environmental risks associated with residual nanomaterials' fate and transport in the environment, are not yet fully explored and understood. Uncertainties of the nature and interaction of nanomaterials in the following areas add to the complexity of risk concerns. These include: uncertainty in relationship between size, surface area, and surface reactivity; and uncertainty in relationship of radionuclides and nanomaterials. A clear understanding of the relationship between these parameters is still evolving and is not yet clearly understood. Additionally, the relation between radionuclides and nanomaterials is not yet determined.

Risk assessment is practiced by EPA and other federal agencies as a tool to evaluate risks associated with chemicals and radionuclides in the environment. Risk assessment approaches and procedures have been formulated by the National Academy of Sciences, and have been subsequently tailored to specific applications by EPA and other federal agencies. EPA risk assessment has four components: hazard identification, toxicity assessment, exposure assessment, and risk characterization. Although the risk assessment paradigm has been used successfully by the scientific community since the early 1980s, its application to nanotechnology requires incorporating an uncertainty in basic knowledge that is very large when compared to the uncertainty for other materials and pharmaceuticals. To do so requires an understanding of product life-cycle and the ability to communicate effectively with personnel, stakeholders, and regulators.

Although risk assessment/management of conventional chemicals is well established, nanotechnology risk assessment is an emerging field; there is a growing body of scientific literature dealing with potential associated risks, including:

- Effects of nano-particle introduction on soil chemistry/fertility/texture;
- Fate and transport (e.g., zero-valent iron (ZVI) or ZVI-uranium-contaminated nano-particles);
- Exposure pathways and assessment (including environmental and occupational exposures, both chronic and acute);
- Dose-response relationship and toxicity (including effects on organs such as lungs, gills, liver, kidneys, and immune systems);
- Bioaccumulation and biomagnification (e.g., food chain); and
- Effects on humans as well as effects on ecosystems, ranging from impacts at molecular (nano) scale through the microbial (microorganisms) and the meso (small animals) to the macro (large animal communities).

The following sections provide a brief overview of: nanomaterial properties potentially associated with risk (1.5.1), possible approaches to nanotechnology risk assessment (1.5.2), data gaps and limitations for assessing nanomaterial risk (1.5.3), and an overview of the proposed frameworks for risk management (1.5.4).

1.5.1 Nanomaterial Properties Associated with Risk

Characteristics of nanomaterials potentially leading to increased toxicity, risks and associated modifying factors have been discussed in recent literature (Biswas and Wu 2005, Borm and Muller-Schulte 2006, Borm et al. 2006, Gwinn and Vallyathan 2006, Kreyling et al. 2006, Medina et al. 2007, Nel et al. 2006, Oberdorster et al. 2007, Thomas and Sayre 2005). In general, the following properties of nanomaterials are discussed as potential risk drivers:

- *Chemical composition* is one of the key factors discussed. Nanomaterials may be derived from bulk materials with known toxic properties. Moreover, in many cases a given nanomaterial can be produced by different processes yielding several derivatives of the same material. It is important to note that the chemical properties of particles at the nanometer size can differ significantly from the chemical properties of larger particles consisting of the same chemical composition.
- *Toxicity potential* can be caused by either chemical toxicity based on chemical composition or stress or stimuli caused by the surface, size, and/or shape of the particle. Differentiation between these two toxic effects is not straightforward (Brunner et al. 2006), but the size of the particle may indirectly dominate the uptake of particles into cells (Limbach et al. 2005, Kreyling et al. 2006).
- *Surface reactivity* can increase the harm caused by nanomaterial in a cell and reduce the potential for environmental degradation (Limbach et al. 2007). Materials with active surfaces are deemed more harmful than the materials that lack such surfaces. It should be noted that smaller particle size also means higher surface reactivity because more of the atoms are in the surface of the particle.

- *Solubility and environmental mobility* have been proven to greatly affect the risk associated with nanomaterials (Brunner et al. 2006). Higher mobility results in higher risk, and insoluble materials or materials with nanoparticles embedded in a bulk material matrix may be less bioavailable.
- *Agglomeration* affects the toxicity as well. Particles that naturally agglomerate into larger units can be interpreted as less toxic. Three agglomeration classes (low, medium, and high) have been defined. In these, highest agglomeration corresponds to lowest risk.

1.5.2 Possible Approaches to Nanotechnology Risk Assessment

Though multiple frameworks for nanomaterials risk assessment and risk management have been proposed, none has been formally adopted as regulatory tool (Linkov et al. 2008). Two examples of the representative risk assessment frameworks are presented in this section, while multiple risk assessment and risk management frameworks are summarized in Section 1.5.5.

NanoRisk Framework

The NanoRisk Framework (www.NanoRiskFramework.com) was developed by DuPont Corporation and the Environmental Defense Fund to address the environmental, health, and safety risks of nanomaterials across all stages of product life cycle. It recommends six distinct steps:

- Step 1. Describe Material and Application. Develop a general description of the nanomaterial and its intended uses, based on information in the possession of the developer or in the literature. The user also identifies analogous materials and applications that may help fill data gaps in this and other steps.
- Step 2. Profile Lifecycle(s). The second step defines a process to develop three sets of profiles—of the nanomaterial's properties, its inherent hazards, and its associated exposures throughout the material's lifecycle. The properties profile identifies and characterizes a nanomaterial's physical and chemical properties. The hazard profile identifies and characterizes the nanomaterial's potential safety, health, and environmental hazards.
- Step 3. Evaluate Risks. In this step, all the information generated in the profiles is reviewed in order to identify and characterize the nature, magnitude, and probability of risks presented by this particular nanomaterial and its anticipated application. In so doing, the user considers gaps in the lifecycle profiles, prioritizes those gaps, and determines how to address them—either by generating data or by using, in place of such data," reasonable worst case" assumptions or values.
- Step 4. Assess Risk Management. Here the user evaluates the available options for managing the risks identified in Step 3 and recommends a course of action. Options include engineering controls, protective equipment, risk communication, and product or process modifications.

- Step 5. Decide, Document, and Act. In this step, appropriate to the product's stage of development, the user consults with the appropriate review team and decides whether or in what capacity to continue development and production. Consistent with a transparent decision-making process, the user documents those decisions and their rationale and shares appropriate information with the relevant stakeholders, both internal and external.
- Step 6. Review and Adapt. Through regularly scheduled reviews as well as triggered reviews, the user updates and re-executes the risk evaluation, ensures that risk-management systems are working as expected, and adapts those systems in the face of new information (e.g., regarding hazard data) or new conditions (such as new or altered exposure patterns).

Through these six steps, the framework seeks to guide a process for risk evaluation and management that is practical, comprehensive, transparent, and flexible.

Comprehensive Environmental Assessment Approach (Davis 2007):

The Comprehensive Environmental Assessment (CEA) approach combines life-cycle perspective with the risk assessment paradigm. This systematic approach could guide research strategy for assessing the risks of nanotechnology and avoid unintended consequences (Davis 2007). The CEA approach begins with assessing product life cycle stages including material production or extraction, manufacturing processes, distribution, storage, use, and disposal (including recycling). At any given stage of the life cycle, nanoscale substances and/or associated materials (e.g., manufacturing by-products) might enter one or more of the environmental media—air, water, soil—and affect humans and ecological receptors through multiple pathways, including food web. It is important to identify nanomaterials in their primary form and, further, to consider the transport and transformation processes they may undergo during the product life cycle.

To evaluate exposure in a comprehensive manner, it is important to consider, among other things, both aggregate exposure across routes (inhalation, ingestion, and dermal absorption) and cumulative exposure to multiple (primary and secondary) pollutants. The CEA approach tends to focus on the range of exposure scenarios, including micro-environmental and high-end exposures, not just "typical" or "average" exposure levels. The human health and ecological hazards associated with respective contaminants can be described qualitatively and, if possible, quantitatively.

1.5.3 Data Gaps and Limitations for Nanomaterials Risk Assessment

Though the use of nanomaterials is increasing, understanding the environmental fate and transport, toxicity, and potential human health and ecological risks associated with nanomaterial use remains extremely limited. This is due to a variety of barriers, including proprietary nature of information; and lack of standardization in nomenclature, metrics, and materials (CRS 2008).

Risk assessment requires information related to the following four components: hazard identification, toxicity assessment, exposure assessment, and risk characterization. For human health and environmental risk assessment of nanomaterials, the current knowledge base contains data gaps. The literature has established these knowns (things we know that we know) and unknowns (things we know that we don't know) in the nanotechnology context for the four components (Davis 2007). Some of the data gaps for each of the risk assessment components are described below.

- *Predicting the environmental fate of nanomaterials*: At present there are few available studies on the environmental fate of nanomaterials but they are not adequate to predict the fate of nanomaterials based on their fundamental properties. Nanomaterials released to soil and ground water as part of remedial activities can be strongly sorbed into soil due to their high surface areas, and therefore become immobile. On the other hand, nanomaterials are small enough to fit into the smaller spaces between soil particles, and therefore might travel farther than larger particles before becoming trapped in the soil matrix. In addition to the nanomaterial properties discussed above, types and properties of the soil and water can affect nanomaterial mobility. Since nanoparticles are likely to be transported as colloids, the mobility of mineral colloids in soils and sediments and the availability of humic substances are important considerations. Additionally, in the presence of various soils having different pH, and radionuclides, nanomaterials may form different byproducts. The fate of nanomaterials in aqueous environments is controlled by solubility or dispersability; interactions between the nanomaterial and natural and anthropogenic chemicals in the system; and biological and abiotic processes. Light-induced photoreactions are often important in determining the environmental fate of chemical substances.

- *Nanomaterial toxicity and bioaccumulation potential*: Past literature provides some evidence of toxicity and bioaccumulation potential, but the results are generally inconclusive. Laboratory testing of nanomaterial uptake has shown a wide range of potential affects on tested organisms, including bioaccumulation potential, mortality, and biomarker-response. Nevertheless, the concentration of nanoparticles used in this and other studies may far exceed concentrations that could potentially result from those that would be associated with site remediation.

- *Exposure estimation:* When a nanomaterial is used for an environmental application, exposure estimation might not be straightforward. Multiple variables could influence nanomaterial exposure assessment, including the characterization of the effectiveness of variations in biological reactivity, size, shape, and charge, as well as factors that complicate the straightforward estimation of exposure such as metabolism, excretion, and adduction to biological molecules. For example, several studies on carbon nanotubes have shown that the toxicity and distribution of nanoparticles is dependent upon the presence of functional groups, impurities, fiber length, and aggregation status.

- *Risk Characterization*: Given estimates of exposure and toxicity, the final step involved in estimating the hazard of contaminant exposure is risk characterization (i.e., the likelihood of adverse environmental impact at varying degrees of exposure). Risk characterization must be developed separately for each nanomaterial, or even for the same nanomaterials with different functions or at different environmental life-cycle stages. Given the required effort, detailed risk characterization may not be possible. Decision tools and databases could be developed to allow the use of all available information, as well as proxy data for making the best judgment on risk characterization.

1.5.4 Approaches to Managing Nanotechnology Risk

As a field of science, nanotechnology is still young and uncertainty in basic knowledge does not lend itself to fully informed and accurate risk assessments, but scientific evidence does exist that suggest some nanoparticles may be hazardous. Some regulatory and industry representatives caution that inadequate government oversight, or even a perceived lack of oversight, could lead to consumer rejection of an entire range of products incorporating nanotechnology. Such a reaction would significantly hinder development and industry growth. To prevent a loss of consumer confidence, academic researchers, policy analysts, and some nanotechnology entrepreneurs have been working with federal agencies that are responsible for protecting the environment, workers, and consumers (CRS 2008).

Assessment and management of the potential risks associated with nanotechnology is a challenge with which U.S. agencies and countries in the European Union (EU) are beginning to come to terms. Despite all the limitations, some progress in approaching risk-based nanotechnology regulation is being made. In the EU for example, the European Commission (EC) has adopted the opinion of the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) on definitions for nanotechnology. This advance takes one of the first steps towards risk assessment and regulation: standardizing nomenclature, metrics, and materials. In addition, the EU is currently conducting research to compare nanotechnology regulatory policies in the EU with those in the United States. Similar to previous efforts to reach coordination on regulation (including beef, chemicals, and genetically modified organism regulations), those involved are hopeful that this research will improve transatlantic regulatory cooperation of nanotechnology in the future (NanoReg News 2008).

A review of current nanomaterial risk management frameworks and related documents is summarized in Table 1. Details of these can be found in the references provided.

Table 1: Current nanomaterial risk frameworks [1]

Agency	Focus	Citation
U.S. Environmental Protection Agency (EPA) White Paper	Comprehensive framework intended to set forth current scientific knowledge and its gaps related to possible environmental benefits of nanotechnology, as well as potential risks from environmental exposure to nanomaterials.	(US EPA 2007)
Federal Drug Administration (FDA)	Report intended to help assess questions regarding the adequacy and application of the FDA's regulatory authority to nanomaterials, and to provide findings and recommendations to the FDA Commissioner.	(US FDA 2007)
Woodrow Wilson Center	Paper intended to describe the possibilities for government action to deal with the adverse effects of nanotechnology, and to provide evidence relevant for determining what needs to be done to manage nanotechnology.	(Davies 2006)
Environmental Defense (EDF)-DuPont	Comprehensive framework for the responsible development, production, use, and end-of-life disposal of nanomaterials, intended for use by companies and other organizations.	(EDF-DuPont 2007)
Québec Commission	Comprehensive discussion of the scientific, legal, and ethical implications of nanotechnology, intended to help uphold the protection of health and the environment, as well as respect for many values such as dignity, liberty, integrity, justice, transparency, and democracy.	(QC 2006)
Royal Society	Comprehensive framework intended to summarize current scientific knowledge and applications of nanotechnology, and	(RS & RAE 2004)

[1] **Linkov, I.**, Satterstrom, K., (2008). "Nanomaterial Risk Assessment and Risk Management: Review of Regulatory Frameworks." In: Linkov, I., Ferguson, E., Magar, V. (in press). "Real Time and Deliberative Decision Making: Application to Risk Assessment for Non-chemical Stressors. Springer, Amsterdam.

Agency	Focus	Citation
	to identify possible health and safety, environmental, ethical, and societal implications or uncertainties.	
Department for Environment, Food, and Rural Affairs (DEFRA)	Trial Voluntary Reporting Scheme to collect data from organizations in the nanotechnology industry to help the United Kingdom develop appropriate controls for risks to the environment and human health from nanomaterials.	(UK DEFRA 2006)
Responsible NanoCode	Paper intended to highlight key issues that emerged from a business workshop on nanotechnology, including development of a responsible nanotechnology code.	(RNC 2006)
European Commission Scientific Commission on Emerging and Newly Identified Health Risks (SCENIHR)	Technical document intended to assess the appropriateness of current risk assessment methodologies for the risk assessment of nanomaterials, and to provide suggestions for improvements to the methodologies.	(EC SCENIHR 2007)
European Commission Action Plan	Plan intended to help Europe build on its strengths and advances to ensure that nanotechnology research is carried out with maximum impact and responsibility, and that the resulting knowledge is applied in products that are useful, safe, and profitable.	(EC 2005)
International Risk Governance Council (IRGC) Policy Brief	Brief intended to assist policy makers in developing the processes and regulations to enable the development and public acceptance of nanotechnology.	(IRGC 2007)
IRGC White Paper 1	Comprehensive framework intended to advance the development of an integrated, holistic, and structured approach for the investigation of risk issues and the governance processes and structures pertaining to them.	(IRGC 2005)
IRGC White Paper 2	Comprehensive framework which applies general IRGC risk governance framework to the field of nanotechnology.	(IRGC 2006)

In response to public concern for the protection of the environment and human health from the potential hazards of nanomaterials, EPA has released a nanotechnology research strategy to protect the environment (EPA 2008). In addition, EPA has also recently completed the Basic Program phase of the EPA's Nanoscale Materials Stewardship Program (NMSP), where some organizations are showing their support for a successful beginning of a voluntary information collection program (NanoReg News 2008).

Currently, the main challenge facing EPA is minimizing nanotechnology's potential for unintended, harmful consequences, while pursuing the positive aspects of nanomaterial use, including potential of environmental remediation applications. In the Office of Research and Development's (ORD) recently released *Draft Nanomaterial Strategy* (EPA 2008), EPA both builds on and is consistent with the NNI's previous reports, as well as its own *Nanotechnology White Paper* (EPA 2007). In *Draft Nanomaterial Strategy*, EPA gives special attention to its mission to protect the environment and its specific needs for being able to regulate nanotechnology (NanoReg News 2008). It also identifies four major areas for future research:

- environmental fate and transport,
- human health implications,
- risk assessment methodology, and
- risk mitigation strategies.

Initially, EPA's research will focus on nanoscale titanium dioxide, ZVI, nanosilver, carbon nanotubes, and cerium oxide, with the intention that the resulting body of knowledge can be extrapolated for classes of nanomaterials in the future, particularly as nomenclature, metrics, and materials become standardized. Anticipated outcomes from this research program are expected to be focused research products that address risk assessment and risk management needs for nanomaterials in support of the various environmental statutes for which EPA is responsible (NanoReg News 2008).

1.6 Nanotechnology for Environmental Remediation

1.6.1 Current Applications

Recent advances in the design, production, and fundamental understanding of nanomaterials have led to preliminary investigations of their use in the remediation of chlorinated organics in the subsurface, and to a wide range of suggestions for their potential use in the remediation of other environmental contaminants, including those at radiologically-contaminated sites. The potential for innovative use is directly related to the enhanced chemical activity resulting from the increased surface area and the manifestation of quantum effects, yet it also takes advantage of a third feature of nanoparticles, namely their ability to be transported to areas inaccessible to other remediation approaches. For example, if we consider bioremediation, part of the promise lies in the fact that microbes capable of destroying organic contaminants can directly access subsurface pore structure that is too small for regular particles to access. However, there is still much of the pore structure in the subsurface that is too small even for

microbes. Nanoparticles are typically two orders of magnitude smaller than bacteria and can thus be transported to an occluded contaminant that is hidden from direct bacterial contact. Current applications, discussed in more detail in Sections 2 and 3 of this document, include zeolites and nanoparticulate ZVI.

1.6.2 Awareness of Potential Environmental Benefits

Since nanotechnology and nanomaterials are comparatively new technologies, only partial knowledge of the environmental fate, transport, effects, and risks associated with them is available, and some of this information appears to be contradictory. Ultimately, this knowledge will be crucial in deciding whether a technology involving nanomaterials is an appropriate remedy. Concerns in this regard have been so strong that a report by the Royal Society (RS) and the Royal Academy of Engineering (RAE) in the United Kingdom has recommended "that the use of free (that is, not fixed in a matrix) manufactured nanoparticles in environmental applications, such as remediation, should be prohibited until appropriate research has been undertaken and it can be demonstrated that the potential benefits outweigh the potential risks (RS/RAE 2004)." Thus, it is important to conduct a comprehensive review and evaluation of both the effectiveness and the potential impacts of available treatment options.

Within all of the discussion about nanotechnology opportunities, consideration of the application of nanotechnology to environmental problems seems to have been subordinated to consideration of risks of nanotechnology. Though the potential has been recognized, often it is the risks posed to human health and the environment that have dominated discussion of nanotechnology and the environment. The term "disruptive technology" was introduced in 2003 (Uldrich and Newberry 2003) to describe a new technology that is significantly cheaper (or performs better) than a current technology, and will revolutionize worldwide markets by superseding the existing technology. The industries on which nanotechnology will likely have a disruptive effect were analyzed and at the high-end (i.e., largest impact) included:

- Healthcare
- Long-term care
- Electronics
- Telecom
- Packaging
- United States Chemical
- Plastics
- Apparel
- Pharmaceutical
- Semiconductor

At the low-end, the industries included:

- Cosmetics
- Chocolate
- Batteries
- Blue jeans

- Khakis
- Fluorescent tagging
- Mouthwash

At the time of Uldrich and Newberry 2003, the environmental industry was not classified on the list.

1.6.3 EPA's Involvement in Nanotechnology

Fortunately, nanotechnology in the environmental industry is progressing, gradually becoming more advanced and better recognized. EPA is obligated to protect human health and safeguard the environment by better understanding and addressing potential risks from exposure to nanoscale materials, but it is also interested in researching and developing the possible benefits of nanotechnology. Since 2001, EPA has played a leading role in funding research and setting research directions for developing environmental applications of nanotechnology. Two recent examples demonstrate EPA's commitment: the "Nanotechnology White Paper" and the "Workshop for Nanotechnology on Site Remediation."

In February 2007, EPA published the "Nanotechnology White Paper" (EPA 2007) based on the work of a cross-Agency workgroup created in December 2004 by EPA's Science Policy Council. It describes key science issues EPA should consider to ensure that society accrues the important environmental protection benefits that nanotechnology may offer. The document notes that since 2001, EPA's Science To Achieve Results (STAR) grant program has funded 36 research grants—totaling nearly $12 million—in the application of nanotechnology to protect the environment, including the development of: 1) low-cost, rapid, and simplified methods of removing toxic contaminants from water; 2) new sensors that are more sensitive for measuring pollutants; 3) green manufacturing nanomaterials; and 4) more efficient, selective catalysts. Additional projects have been funded through the Small Business Innovation Research (SBIR) program, and there are 14 recent STAR program projects focused on studying the possible harmful effects, or implications, of engineered nanomaterials.

This white paper also describes the benefits, risk assessment, and responsible development of nanotechnology, and outlines the involvement in nanotechnology by various EPA Offices including:

- *Office of Pollution Prevention and Toxics (OPPT)* — activities include reviewing premanufacture notifications for a number of nanoscale materials that have been received under the Toxics Substances Control Act, initiating a Nanoscale Materials Stewardship Program to encourage submission and development of information for nanoscale materials (see http://www.epa.gov/oppt/nano/stewardship.htm), public outreach, and international engagement on nanotechnology issues with the Organization of Economic Cooperation and Development and International Organization for Standardization (ISO).

- *Office of Air and Radiation/Office of Transportation and Air Quality (OAR/OTAQ)* — activities include reviewing an application for registration of a diesel additive containing cerium oxide. Cerium oxide nanoparticles are being marketed in Europe as on- and off-road diesel fuel additives to decrease emissions, and some manufacturers claim fuel economy benefits.
- *Office of Pesticide Programs (OPP)* — activities include working with members of the pesticide industry regarding licensing/registration requirements for pesticide products that utilize nanotechnology.
- *Office of Solid Waste and Emergency Response (OSWER*) — activities include investigating potential implications and applications of nanotechnology by such means as: an October 2005 workshop on "Nanotechnology for Site Remediation" organized with EPA's ORD and several other federal agencies; and a July 2006 symposium entitled, "Nanotechnology and OSWER: New Opportunities and Challenges."
- *Office of Enforcement and Compliance Assurance (OECA)* — activities include reviewing Agency information on nanotechnology (e.g., studies, research); evaluating existing statutory and regulatory frameworks to determine the enforcement issues associated with nanotechnology; evaluating the science issues for regulation/enforcement that are associated with nanotechnology, and; considering what information OECA's National Enforcement Investigations Center (NEIC) may need to consider to support the Agency.

Importantly, EPA's white paper presents a set of key nanotechnology recommendations, including:

- **Environmental Applications Research.** The Agency should continue to undertake, collaborate on, and support research to better understand and apply information regarding environmental applications of nanomaterials.
- **Risk Assessment Research.** To ensure that research best supports Agency decision-making, EPA should conduct case studies to further identify unique risk assessment considerations for nanomaterials. The Agency should also continue to undertake, collaborate on, and support research to better understand and apply information regarding nanomaterials':
  - o chemical and physical identification and characterization,
  - o environmental fate,
  - o environmental detection and analysis,
  - o potential releases and human exposures,
  - o human health effects assessment, and
  - o ecological effects assessment.
- **Pollution Prevention, Stewardship, and Sustainability.** The Agency should engage resources and expertise to encourage, support, and develop approaches that promote pollution prevention, sustainable resource use, and good product stewardship in the production, use, and end-of-life management of nanomaterials. Additionally, the Agency should draw on new, "next generation" nanotechnologies to identify ways to support environmentally beneficial

approaches such as green energy, green design, green chemistry, and green manufacturing.

- **Collaboration and Leadership.** The Agency should continue and expand its collaborations regarding nanomaterial applications and potential human health and environmental implications.
- **Intra-Agency Workgroup.** The Agency should continue to convene a standing intra-Agency group to foster information sharing on nanotechnology science and policy issues.
- **Training.** The Agency should continue and expand its nanotechnology training activities for scientists and managers.

Another recent example of EPA's involvement in using nanotechnology for better environmental remediation is the October 2005 "Workshop on Nanotechnology for Site Remediation" (EPA 2005). This workshop explored the place of nanotechnology among existing remedial techniques, considered the overall state of the science, and examined some case studies (primarily of nanoparticulate ZVI). Workshop participants also discussed research needs and data gaps. Their findings may be summarized into four broad categories (i.e., performance; toxicity; basic nanoscience; and fate and transport) as follows:

<u>Performance</u>

- Better understanding of injection techniques and control of nanoparticle movement in the subsurface; better ways to overcome other limitations on material emplacement such as permeability changes over time with injections;
- Development of a set of performance-assisting tools such as validation methods, modeling, scale-up equations, statistics, and QA/QC approaches;
- Development of performance metrics/standards of the nanoparticles, including manufacturing, size, shape, storage, and property and reactivity standards for nanoparticles;
- Development of performance assessment and performance prediction tools for the contaminants being remediated;
- Development of in-situ sensors, real-time techniques, and analytical methods for detecting nanoparticles;
- Better understanding of the effects of treatment trains (options and optimization of combinations) and synergies of multiple contaminants "cocktail treatment";
- Need national test sites covering major geologic settings to permit rigorous field demonstration; and
- Need for contingency ability to remove nanoparticles from wastewater and drinking water.

<u>Toxicity</u>

- Recognizing gaps in data and in the understanding of toxicological effects on humans, flora, and fauna and how low risk toxicity can be measured in the environment;
- Recognizing lack of information on fate, stability, and potential for transformation (for example heavy metal sequestration);

- Understanding the difference between maximizing remedial effects while minimizing toxicological problems;
- Integrating toxicological behavior into risk-based decision making; and
- Better understanding of macro-scale toxicity properties and whether it can be extrapolated to nano-scale using knowledge of size, shape, chemistry.

Basic Nanoscience

- Discovering the existence of intrinsic nano-scale processes and mechanisms (such as surface area versus electronic effects and bulk properties versus surface effect);
- Discovering the difference between extrapolating macro-scale and micro-scale to nano-scale, or determining if there is there a unique nano-scale physico-chemistry that cannot be identified at the macro-scale;
- Better understanding needed of agglomeration behavior to control both in-situ reactivity and transport; and
- Recognizing the need for better information products and information synthesis.

Fate and Transport

- Major risks and uncertainties seen in fractured media and in the transport of sequestered contaminants;
- Better monitoring and detection techniques are needed for fate and transport as well as for performance studies; and
- Need much better information on site-to-site variability of fate and transport rather than assuming that behavior identified at one site can be applied widely;

Investigation of fate and transport of nanoparticles for environmental applications is important since an understanding in this area is critical to evaluating performance (the need to know how far and in what form the nanoparticle will travel to perform its function), toxicity (the risk of the nanoparticle traveling unanticipated distances in very toxic forms), and cost (directly related to performance). Though the fate of the nanoparticle will depend heavily on the characteristics and material of the nanoparticle, recent work has indicated that transport may not be as grave a concern as once thought. It has been noted that the common assumption that nanoparticles will be highly mobile in porous media due to their tiny size in comparison with pore spaces, is an oversimplification (Tratynek 2006). The mobility of nanoparticles in the saturated subsurface is the product of the number of nanoparticle collisions with the porous medium per unit transport distance (where collisions arise from Brownian diffusion, interception and gravitational sedimentation) and the sticking coefficient. Calculations for a typical subsurface using a range of sticking coefficients indicates that transport will range from millimeters to a few tens of meters. These calculations seem to have been borne out in field tests with iron nanoparticles used to remediate chlorinated organics.

In fact, an area of current interest is how to coat particles so that they will not stick and will travel further to attain their remedial purpose. This indication of limited travel only applies in porous media and would not be expected to hold in fractured geologic media or in surface water. As a result, EPA is continuing investigations of fate and transport

through research[2] such as that on the environmental fate of single-walled carbon nanotubes in the estuarine environment at the University of South Carolina. Similar work on environmental fate and transport is also being conducted at a number of academic centers, such as the Center for Biological and Environmental Nanotechnology (CBEN) at Rice University, which aims to understand and manipulate the wet/dry interface between nanosystems and biological systems, and the Nanomaterials in the Environment, Agriculture, and Technology Organized Research Unit (NEAT-ORU) at the University of California Davis, which emphasizes research on the interaction of materials and the natural and man-made environment.

1.6.4 International Involvement in Nanotechnology

The United States is not alone in exploring the benefits of nanotechnology for environmental remediation and its implications on human health, welfare, and the environment. Two recent reports from Europe help paint a picture of current thinking.

A 2007 report from the United Kingdom's Department for Environment, Food and Rural Affairs (DEFRA) titled "Environmentally Beneficial Nanotechnologies: Barriers and Opportunities" (Walsh 2007), was commissioned to provide an overview of the areas where nanotechnology could have a beneficial environmental impact above current technology and the barriers preventing its adoption. Five nanotechnological applications were subject to detailed investigation: fuel additives, solar cells, the hydrogen economy, batteries, and insulation.

A workshop on "Nanotechnologies for Environmental Remediation" (Rickerby and Morrison 2007) was convened at the Joint Research Center in Ispra, Italy in 2007. This workshop brought leading scientists together from across the EU to present their latest work in environmental remediation and discuss issues including:

- The most effective nanotechnologies for pollution prevention or cleanup;
- The dependability and proximity to market of remediation techniques based on nanotechnologies;
- The additional research needed to exploit the full potential of nanotechnology for remediation;
- The most promising environmental nanotechnologies and those that should be further explored;
- The potential risks of using nanotechnologies in remediation applications.
- Whether there is a need for targeted funding for infrastructure to support nanotechnologies for environmental remediation; and
- The opportunities for setting up EU collaborative projects on environmental nanotechnologies.

The issues of environmental remediation were considered to be quite substantial and poorly addressed by conventional technologies. They include access to clean drinking

[2] ORD STAR

water; removal of airborne pollutants; and the cleanup of industrially-contaminated sites (in particular ex-military sites). Although there have been a number of laboratory demonstrations of nanotechnology applications for environmental cleanup, there remains the issue of translating these into industrial-level processes. The workshop consisted of two principal sessions: "Water Treatment and Purification," and "Air, Water and Soil Decontamination." Participants discussed the following important issues:

- Photocatalytic treatment of water for degradation of pollutants and the destruction of microorganisms;
- Titanium dioxide (TiO_2) nanopowder immobilization on substrates to produce a photogalvanic system with a photoanode for photodegradation of organic pollutants;
- Photocatalytic inactivation of bacterial spores and photocatalytic disinfection of water;
- Membrane nanofiltration for the treatment of process and wastewater;
- Colloidal and interface chemistry;
- Development of a system utilizing iron-precipitating bacteria to co-precipitate;
- Organic and inorganic pollutants, such as arsenic;
- Sol-gel synthesis of nanosized TiO_2 particles on polypropylene fibers for the photocatalytic degradation of organic pollutants;
- Ultra nanocrystalline diamond used as an electrode for water treatment and disinfection;
- Feasibility of a Lab-on-a-Chip (LOC) device for analyzing highly radioactive solutions;
- Development of catalytic trap technology and advanced systems for particulate matter;
- Incorporating TiO_2 in building materials or surface coatings to impart self-cleaning and de-polluting properties; and
- A double skin sheet reactor (DSSR) for water purification.

1.7 Nanotechnology for Environmental Remediation of Radionuclides

1.7.1 Technical Status

Discussion in Section 1.6 has illustrated that research of radionuclide remediation is lacking in the growing interest of environmental nanotechnology. The mention in Section 1.6.4 of investigating the feasibility of an LOC device for analyzing highly radioactive solutions is an encouraging exception. In spite of this current situation, the potential for nanotechnology to assist with the remediation of radionuclide-contaminated sites is considerable. For example, zeolites, nanostructured materials that can also be made as nanoparticles, already have a long history of use in the treatment of liquid radioactive waste. ZVI nanoparticles, a reducing agent already implemented for the remediation of chlorinated organics in groundwater, are an excellent prospect for use as a reducing agent to precipitate uranium form contaminated groundwater. LOC is a recently emerged sensing technology that is being actively investigated for modification to radionuclide sensing. The Self-Absorbed Monolayers on Mesoporous Supports (SAMMS) technology,

originally developed by DOE primarily for mercury, but also with radionuclides in mind, has recently had its first field implementation.

In addition to these examples of current or near-term applications of nanotechnology to radionuclides, it is clear from the analysis of the scientific and engineering principles that other technologies can be developed, and it is clear from analysis of broader governmental and industrial issues and initiatives that a rational approach to design of nanomaterials and nanotechnologies is being pursued. Two examples, one technical (rational design of organic ligands) and the other programmatic (Chemical Industry R&D Roadmap for Nanomaterials by Design) demonstrate the potential of a rational design approach.

1.7.2 Rational Approach to Design in Nanotechnology

The rational design of complexants or sequestrants in organic chemistry draws on expertise from a number of areas of chemistry, including supramolecular chemistry, molecular recognition, host-guest chemistry, molecular mechanics, and molecular modeling. The conceptual origins go back over 100 years to the idea developed by Emil Fischer, who proposed that enzyme-substrate interactions occur through a "lock and key" mechanism. Subsequent research was stimulated by work such as the elucidation of DNA structure, where non-bonding interactions were critical to understanding the three-dimensional structure. As far back as the mid to late 1990s, government and industry began shifting their focus in the area of separations from complexants and sequestrants to separations platforms such as membranes. The U.S. chemical industry presents one of the best examples of this structured approach. The U.S. chemical industry is the world's largest, accounting for over 26% of global chemical production (over $450 billion per year) (DOE 2007). The chemical industry worldwide is the largest component of the nanotechnology industry; worldwide the nanotechnology industry is estimated at $130 billion (Cientifica 2007), of which the chemical industry accounts for approximately $69 billion (53%). With its enormous scientific and engineering basis (accounting for one out of every four U.S. patents) and knowledge of varied product requirements, the chemical industry is well positioned and motivated to explore a rational approach to nanotechnology.

Currently, much nanomaterial development occurs through empirical or Edisonian R&D, in which a nanomaterial structure with interesting properties is discovered, an application is subsequently sought and development of a product retaining the nanoproperty is attempted. This approach is hit or miss. As a result, a smaller-than-optimal number of products are produced even though time-to-market can be rapid. Against this background, in 2003, the Chemical Industry Vision2020 Technology Partnership (Vision2020) issued its technology roadmap, "Chemical Industry R&D Roadmap for Nanomaterials by Design: From Fundamentals to Function (Chemical Industry Vision2020 2003)."

Vision2020 is an industry-led partnership process among public and private sector stakeholders in the chemical and allied industries. The chemical industry has recognized both the significance of nanomaterials to its operations and markets and a solution-

oriented approach to materials development, or "nanomaterials by design", is needed. Conceptually, nanomaterials by design is the ability to employ scientific principles in deliberately creating structures with nanoscale features (e.g., size, architecture) that deliver unique capabilities for target applications and require detailed understanding of science at the nanoscale. The general concept of rational design originated within the chemical community after it found early applications in pharmaceutical design. Vision2020's roadmap presented four major research areas for nanotechnology development:

- Manufacturing and Processing—developing unit operations and robust scale-up and scale-down methodologies for manufacturing, with emphasis on synthesis, separation, purification, stabilization, and assembly.
- Characterization Tools—developing analytical tools for measuring and characterizing nanomaterials both in scientific research and in numerous areas of production.
- Fundamental Understanding and Synthesis—developing new paradigms for the creation and controlled assembly of nanoscale building blocks, based on an understanding of physics and chemistry at the nanoscale.
- Modeling and Simulation—developing computational tools to predict bulk properties of materials that contain nanomaterials and can bridge between scales from atoms, to self-assembly, to devices.

Once these developments are achieved, large numbers of diverse products could rapidly enter global markets to solve long-standing problems and stimulate economic growth for decades to come. A library of nanomaterials and synthesis techniques could be established by 2020 for use by material producers and end-users worldwide, offering diverse, high-quality nanomaterial building blocks with well-characterized compositions, stable architectures, and predicted properties. Safe, reproducible, cost-effective, and clearly-defined manufacturing and assembly methods would be available to incorporate nanomaterials into systems and devices designed to perform specified functions, while retaining nanoscale attributes. The roadmap suggests a twenty-year period for the completion of this development.

1.8 Structure of This Report and Summary of Examined Technologies

The remainder of this report is organized into three sections listed below:

- Section 2: Nano-Enabled Remediation Technologies (each technology description is followed by references specific to that technology)
- Section 3: Nano-Enabled Sensor Technologies (each technology description is followed by references specific to that technology)
- Section 4: Observations and Conclusions

Table 2 below provides a summary of the technologies examined in this document and includes a reference to the section in which the technology is discussed, a brief summary of the technology, an estimate of the maturity level for the technology and the main medium in which the technology operates.

Table 2: Summary of Examined Nanotechnologies and Nanosensors

Technology	Section	Summary	Maturity	Media
Zero-valent Iron (ZVI) Nanoparticles	Section 2.2 Page 32	ZVI nanoparticles are a nanotechnology modification of the established ZVI technology in which the ZVI undergoes oxidation and consequently is able to reduce species, such as chlorinated organics and higher valency toxic metals (e.g., uranium and chromium).	The use of macro-scale ZVI in subsurface permeable reactive barriers is a well-established technology. Nano-scale ZVI has already undergone field demonstrations.	Aqueous
Self-Absorbed Monolayers on Mesoporous Supports (SAMMS)	Section 2.3 Page 39	SAMMS is a separations technology designed for the removal of soluble species in aqueous solution. It is likely to be a strong competitor to conventional ion exchangers, solid-supported complexants, or other solid sorbents. The fundamental scientific underpinnings make SAMMS an extremely flexible separations technology.	Commercially available and being used in the field for mercury remediation, with ongoing development for a wide range of toxic and radioactive metals.	Aqueous
Nanofiltration Membranes	Section 2.4 Page 46	Nanofiltration and reverse osmosis membranes are a mature separation technology designed for the removal of particulate and soluble species in aqueous solution. They occupy the part of the spectrum of filtration technologies where extremely small particulates and soluble species can be removed from aqueous solution.	Conventional nanofiltration and reverse osmosis membranes are well-established. The use of insights from recent nanotechnology developments for improved membranes is well underway and commercial products are expected to be available in the near future.	Aqueous
Zeolites	Section 2.5 Page 58	Zeolites are a well-established ion exchange technology that is used, among a wide range of other, non-separatory industrial applications, for the treatment aqueous waste streams containing radioactive solutes. Zeolites are a nanotechnology that had	A mature, long-established technology, widely used for the treatment of radioactive waste streams and under ongoing development.	Aqueous/ soils

Technology	Section	Summary	Maturity	Media
		established uses predating the general concept of nanotechnology.		
Other Nanoparticles	Section 2.6 Page 69	Nanodiamonds, dendrimers, and the Argonne Supergel are presented to demonstrate the range of possibilities offered by nanoparticles— particularly the ease with which a nanoparticle can be incorporated into another technology application and the ability to engineer specific properties into a nanoparticle at the atomic level.	Various depending on specific technology.	Various depen-ding on specific techno-logy.
Uranium Reduction by Bacteria	Section 2.7 Page 77	By using the appropriate micro-organism and nutrient addition, soluble uranium (VI) can be converted in-situ to much less soluble uranium (IV) by enzymatic reduction.	The technology concept is mature and commercially available.	Aqueous, soil, sub-surface
Carbon nanotubes (fullerenes)	Section 2.8 Page 85	A class of hollow, spherical, or ellipsoidal molecules composed entirely of carbon atoms in a cage-like structure. They have a range of potential applications, from sensing elements, to components of advanced nano-composite materials that may enable better membranes for reverse osmosis and nanofiltration.	Nanotubes are now commercially available in "tons-per-year" quantities. Applications are in the laboratory stage with future development likely to speed up now that availability has been increased and cost decreased.	Aqueous
Lab-on-a-Chip (LOC)	Section 3.2 Page 99	LOC is a platform that can integrate a number of laboratory analytical functions, such as separations and analysis of components of a mixture, on a single microprocessor chip using fluid volumes in the nanoliter and lower range, thus allowing realization of small, portable equipment.	The technology is commercially available for biological research.	Aqueous
Microcantilever Sensors	Section 3.3 Page 103	A microcantilever is an extremely small beam supported at one end and capable of well-defined bending and vibrational	The technology concept is mature and commercially available.	Aqueous

Technology	Section	Summary	Maturity	Media
		behavior that can be accurately monitored. When the microcantilever surface is modified so as to be able to bind a target species, the changes in vibrational behavior allow concentration of the target species to be determined.		
Spectroscopic Sensors	Section 3.4 Page 109	Spectroscopic measurements, particularly fluorescence spectroscopy, are one of the most sensitive conventional detection technologies, routinely going to the single molecule level in the laboratory. Nano-enabled technologies promise to expand the availability and application of these techniques. Probe Encapsulated by Biologically Localized Embedding (PEBBLE), surface plasmon resonance, nanobelts and nanorods are discussed as examples.	Various, depending on specific technology.	Primarily aqueous
Nanowire Sensors	Section 3.5 Page 117	Nanowires are solid, rod-like materials with diameters in the 5-100 nm range and are most often made from metals or semi-conducting metal oxides. Their main application is expected to be in sensors, with the underlying phenomenon that is exploited being the field effect upon which field effect transistors are based.	Early stage of development.	Aqueous
Nanobelts and Nanorods	Section 3.6 Page 122	Nanobelts are a class of nanostructure often viewed as a type of nanowire. Nanobelts form ribbon-like structures with widths of 30-300 nm, thicknesses of 10-30 nm, and lengths in the millimeter range. Nanorods are solid nanostructures morphologically similar to nanowires but with aspect ratios of approximately 3-to-5.	Under investigation for various applications.	Various depen-ding on specific techno-logy.

This report does not address technologies complementary to radionuclide remediation or sensing. For example, if a subsurface plume were to contain both Resource Conservation and Recovery Act (RCRA) organics and radionuclides as contaminants, the material was brought to the surface, and a problematic mixed waste was produced; a nanotechnology that could destroy the RCRA organic would accomplish much in assisting with the management of the radionuclide. Though this type of consideration is beyond the scope of this report, it represents yet another approach by which nanoparticles can assist in the management of radionuclide problems.

In addition to the technologies that are presented in this report, there are a number of other technologies or scientific concepts that over the short term, as nanotechnology advances, may have remedial potential for radionuclides. The prediction of future technology success is a task always fraught with risks, particularly as the time period of the prediction grows. It is often pointed out that at the end of the nineteenth century many scientists believed that all of the basic fundamental principles governing physics and chemistry were known, and that few big discoveries left with only details remaining. The difficulties in technical prediction still remain. Some of the choices for the following sections are obvious. For instance, technologies such as ZVI nanoparticles, SAMMS, and zeolites have already found commercial or near-commercial applications in the treatment of radionuclides. Others are included since they are being actively researched for closely similar applications. For instance, dendrimers are being examined for application in the treatment of heavy metals and the transfer of understanding from heavy metals to radioactive metals is usually fairly straightforward; it is very common in research to use the lanthanides as models for the actinides since the non-radioactive lanthanides are much easier to work with than the radioactive actinides and useful predictions and extrapolations of behavior from one class to the other can be made. For the rest of the technologies common factors employed in the analysis of technology potential were used. For example, factors such as the existence of a standardized framework or platform within which to work, the existence of a wealth of related knowledge and supporting research, the technology offering a technically elegant or conceptually compelling solution to a problem, or the robustness and flexibility of a technology are all positive indicators of its likely success. The reader should of course understand that, particularly in a rapidly developing field, there is always inherent uncertainty in making extrapolations of likely technology success.

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2.0 Nano-Enabled Remediation Technologies

2.1 Introduction

In dealing with the remediation of environmental contamination or the closely-related concern of managing wastes, options for treating non-radiological (though potentially very hazardous) materials can be divided into two broad categories: separation of the contaminant and transformation of the contaminant. For example, if an aqueous stream is contaminated with trichloroethylene (TCE), the stream could be cleaned by passage through a bed of activated charcoal to separate the TCE from the stream, or by passage over a bed of ZVI, in which case the ZVI would transform the TCE. In the case of radionuclide contamination, the situation is complicated by the fact that no amount of transformation will ever remove the radiological characteristic of the waste—a uranium atom will always remain a uranium atom no matter how it speciates chemically. Transformations may be useful, but only to the extent that they assist in bringing about a separation. For radiological contamination, the separations of interest may be the removal of the radioactive species from its host matrix (i.e., an extraction), or it may involve processes such as fixation or stabilization, in which the radioactive material is separated from any mobilization and/or transport pathways so that the risk it poses is reduced or eliminated altogether by preventing it from being made available to a receptor.

The remediation of radionuclide-contaminated sites has been problematic for decades. Radionuclides typically remain a matter of concern even at concentrations that are orders of magnitude lower than those for most non-radiological materials. Further, the geological matrix can present considerable heterogeneities even over small distances and is inherently difficult to characterize. The situation is further complicated by the timeline for developing remedial technologies. In contrast to enabling technologies such as sensors, remedial technologies are generally much more time-consuming and involve considerably higher costs and risks. These problems are amplified when radionuclides are involved. Though the novel chemical and physical properties offered by nanoparticles may yield new approaches to remediation, the fundamental difficulties posed by radionuclides will not disappear. This does not mean that nanoparticles offer little promise for environmental remediation. On the contrary, the potential appears to be great, but it is more likely to come in the areas of remediation of non-radiological contaminants, pollution prevention through the development of greener manufacturing processes, better waste treatment of non-radiological contaminants, and sensors than in the area of remediation of radiological material.

Having provided this cautionary background, the research involved in preparing this report indicates that nanotechnology is likely to provide some useful tools for the toolbox of remediation technologies applicable to radionuclide-contaminated sites. For the past two decades, it has been recognized that environmental contamination by radionuclides constitutes one the most difficult environmental problems. The cost of remediation of such sites may be enormous. Major decreases in anticipated costs do not seem to be likely through incremental improvements to existing approaches and transformational alternatives that have been actively sought. Since nanotechnology is still in its infancy,

the possibility of transformational approaches arising should not be dismissed, even if there is little indication at present regarding how this will come about.

Already, nanotechnology does offer some intriguing possibilities. One example is that macroscale ZVI has been used successfully for years as a means of treating chlorinated organics in groundwater via use of permeable reactive barriers (PRBs). Nanoscale ZVI is currently being investigated for the same application, exploiting the fact that its rheological properties allow it to be injected. ZVI has also been investigated as a reductant to transform materials of concern, such as chromium and uranium, from their higher valency, more soluble forms, to lower valency, and soluble forms possessing lower risk. It seems likely that nanoscale ZVI may offer the same chemical reductant properties, possibly even enhanced, with the flexibility of injectability. This conclusion involves an extrapolation, but it is a fairly small one. A second example, and one that does not involve an extrapolation, is zeolites—nanostructured, ion-exchanging separations materials that have been used in radioactive material waste management for half a century. A third example is the Self-Assembled Monolayers on Mesoporous Supports (SAMMS) technology, which offers a new platform for separations agents. This technology is currently being demonstrated for mercury removal and, in combination with the fundamental understanding already available, the extrapolation to a technology for the separation of radionuclides is small.

Separations may be the area where nanotechnology makes its biggest impact in remediation. Carbon nanotubes can be incorporated into membranes and permit extremely fast fluid flow; they are under active investigation as a desalination technology. The combination of existing knowledge on ligand design—an area of fundamental importance to separations science—with new nanostructures, such as dendrimers, may offer greatly improved separations performance. The following sections describe technologies or technology concepts that have either been demonstrated for radionuclide treatment, such as zeolites, or that can be comfortably extrapolated to radionuclides, such as ZVI. Since a certain degree of extrapolation is necessarily involved, the survey in this report is not intended to be comprehensive, but rather seeks to provide information on reasonable possibilities that may yield technologies in the near future. The technologies examined in this report are:

- ZVI nanoparticles
- SAMMS
- Membranes: nanofiltration and affinity
- Zeolites
- Other nanoparticles
- Uranium reduction by bacteria
- Carbon nanotubes

2.2 Zero-valent Iron Nanoparticles

2.2.1 Background

The massive surface area and unique properties of nanoparticles have led to much research on their application to environmental remediation. Across the broad array of environmental concerns, research ranges from the use of TiO_2 nanoparticles for photocatalytic treatment of nitrous oxides in plant emissions, to the use of naturally occurring metal oxide nanoparticles for the treatment of organic contaminants in groundwater. There are, however, few examples of commercial-scale technologies that use nanoparticles for environmental remediation of non-radiological materials, and even fewer for remediation of radionuclides. The closest example to a commercial technology is the use of iron nanoparticles as a reductant for the remediation of chlorinated organics in water; this is a direct modification of the use of iron filings or microscale iron powder for the remediation of chlorinated organics in water. In addition, one company (Pars Environmental Inc.) has successfully used iron nanoparticles at several chromium-contaminated sites for reducing soluble and carcinogenic chromium in the +6 valence state to insoluble and non-carcinogenic chromium in the +3 valence state.

In general, nanoiron particles can treat the following contaminates in a range of geological settings:

- Contaminants:
  - Halogenated aliphatics (PCE, TCE, 1,1,1-TCA, 1,1,2,2-TeCA)
  - Halogenated aromatics
  - PCBs
  - Halogenated herbicides and pesticides
  - Nitroaromatics
  - Metals (e.g., Cr^{6+}, As)
- Geologic Conditions:
  - Sand
  - Silt
  - Fractured rock
  - Landfills
  - Fill materials
  - Sediments

Additionally, EPA is preparing a fact sheet on the use of nanotechnology for site remediation and will include information about sites where the technology has been tested.

2.2.2 Description

Iron nanoparticles represent the only field application of free-released nanoparticles for environmental remediation. First suggested in 1996 and now the subject of a number of

reviews (Kumar 2006, Zhang and Elliott 2006, Lo et al. 2006), the use of iron nanoparticles is a variation on the use of ZVI as a PRB.

The non-nanoparticle ZVI PRB technology has been used to remediate contaminated groundwater for almost 20 years (Senzaki and Kumagai 1988) and has been demonstrated in the field and in the laboratory for a wide range of contaminants, including the reduction of nitrates, bromates, chlorates, nitroaromatic compounds, chlorinated ethanes, chlorinated methanes, and brominated or carbarylated pesticides, and the removal of arsenic, lead, uranium, mercury, and hexavalent chromium (Nuxoll et al. 2003, Arnold and Roberts 2000). Typically, iron filings or microscale iron powder have been used to create a barrier a few meters wide, contained by gravel supporting beds. The chemistry is well understood as the corrosion of iron based on the following reactions:

$$2Fe^{0}(s) + 4H^{+}(aq) + O_2(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$$Fe^{0}(s) + 2H_2O(l) \rightarrow Fe^{2+}(aq) + H_2(g) + 2OH^{-}(aq)$$

$$4Fe^{2+}(aq) + 4H^{+}(aq) + O_2(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l)$$

$$2Fe^{2+}(aq) + 2H_2O(l) \rightarrow 2Fe^{3+}(aq) + H_2(g) + 2OH^{-}(aq)$$

As ZVI is oxidized to ferrous and/or ferric iron, pH increases, hydrogen is evolved, oxidizable materials are consumed, and the strong reducing conditions created are favorable for the pathways (oxide-mediated electron transfer from the metal to the chlorinated organic, reduction of the chlorinated organic by the ferrous iron and reduction by evolved hydrogen)—leading to complete dechlorination. Eventually, ferric or ferrous iron may precipitate as a solid or remain in solution, depending on the pH and redox conditions. Mineral precipitates of carbonates, sulfides, and/or oxides may form coatings on the reactive grains, inhibit the performance of the iron, and reduce the porosity and permeability of the aquifer, but analysis of the evidence suggests that destruction of chlorinated solvents can still continue to completion. Additionally, the generation of strong reducing conditions and hydrogen gas foster anaerobic microbial growth and increase natural biological degradation in the field (Henn and Waddill 2006).

The first field-scale application of conventional ZVI for groundwater remediation was at the Canadian Forces Base in Borden, Ontario in 1991. A treatment zone was excavated, isolated by sheet pile; filled with a mixture of granular iron and sand; and the sheet piles were removed. Contaminated groundwater flowed through the treatment zone and the chlorinated ethenes (perchloroethylene and trichloroethylene) were almost completely removed. The approach is now a standard, and regulatory guidance for the general use of PRBs (including those involving iron) is available (ITRC 1999a), together with design guidance (ITRC 1999b), and recently learned lessons and new directions (ITRC 2005).

The concept of using nanoparticle iron to remediate chlorinated organics follows almost immediately from the conventional ZVI treatment. The small size of the particles (~10 nm) would allow them to be injected into a geologic matrix and reach areas unavailable even to the microbes (~1,000 nm) used in bioremediation. Since reactivity appears to be

a direct function of total iron particle surface area, their performance is expected to be superior to that of larger particles. Production of ZVI nanoparticles is relatively easy, involving the reduction of ferric ion by sodium borohydride (Wang and Zhang 1997):

$$4Fe^{3+} + 3BH^{-}_{4} + 9H_2O \rightarrow 4Fe^{0}\downarrow + 3H2BO^{-}_{3} + 12H^{+} + 6H_2$$

A successful, pilot-scale study has already been performed (Henn and Waddill 2006) using 300 pounds of palladium-catalyzed and polymer-coated nanoscale ZVI particle suspension at the Naval Air Station in Jacksonville, Florida. The particle suspension was injected via a gravity feed and recirculated through a source area containing chlorinated volatile organic compounds (VOCs). Between 65 and 99% aqueous-phase VOC concentration reduction occurred, due to abiotic degradation, within five weeks of the injection and then yielded to slower biological degradation. Aqueous-phase VOC concentrations were reduced up to 99 % and were near or below applicable regulatory criteria. Though there are still considerable knowledge gaps, the technology appears to have great potential.

Recently, Pars Environmental, Inc. has developed a ZVI particle which, over time, encapsulates the metal contaminant; it is reported that this encapsulated layer immobilizes the contaminant for up to 30 years. This stepwise process resulting in the reduction of Cr(VI) to Cr(IV) and encapsulation of Cr(IV) in an onion-like skin around a nano ZVI particle is illustrated in Figure 1.

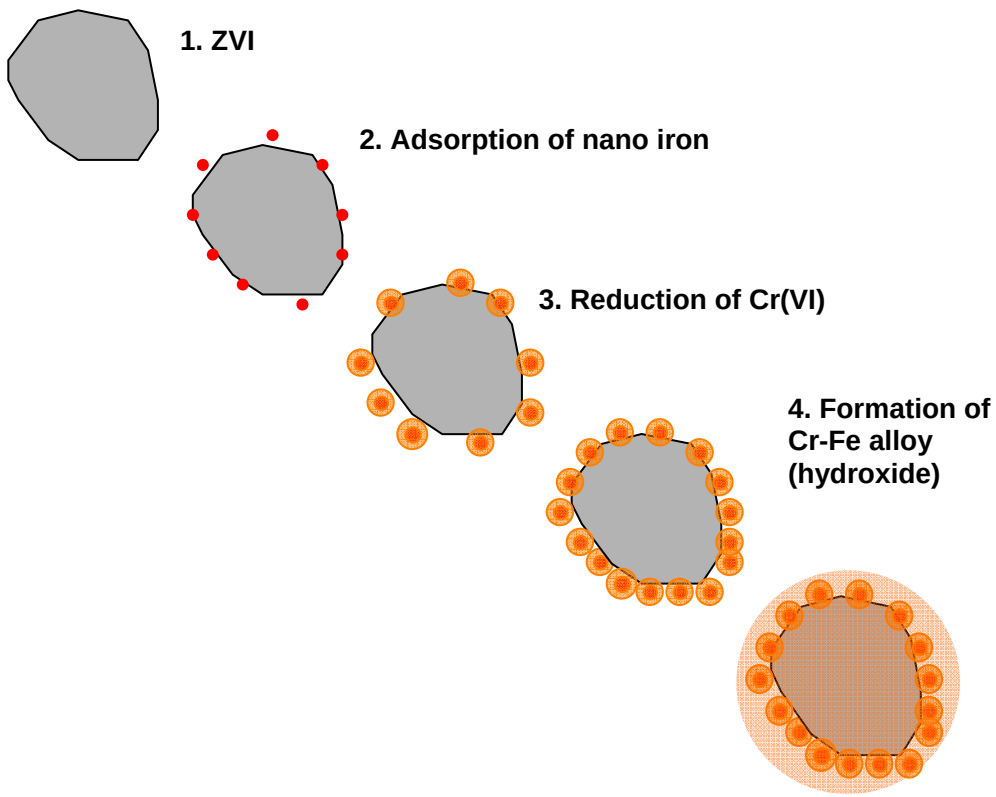

Figure 1. Encapsulation stabilization of the contaminant

The key features of this process as illustrated for Cr(IV) are:

1. Nano Cr-Fe layer
    a. Thickness - 10 nm
    b. ~ 40 atoms
2. 2/3 of the mass from Cr(VI)
    a. Cr 0.667 Fe 0.333 OOH
3. Insoluble
4. Reducing power (Fe0)

The same reducing ability of ZVI is suggested for the remediation of radionuclides and heavy metals to bring about a reduction of the metal to a less soluble, lower oxidation state. For chromium, a conventional ZVI PRB consisting of 450 tons of granular ZVI was installed in 1996 at the United States Coast Guard Support Center in Elizabeth City, North Carolina, and has been subject to considerable documentation (Puls et al. 1998, Blowes et al. 1997, Blowes et al. 1999, FRTR 1998). The PRB was a continuous trench approximately 46 m long, 7 m deep, and 0.6 m thick. Concentrations of Cr(VI) had been as high as 5 mg/L, but decreased to non-detectable levels (<0.0025 mg/L) after installation of the PRB. The removal mechanism for Cr(VI) was determined to be precipitation as Cr(III) oxyhydroxide or co-precipitation with iron oxyhydroxide. Despite this success, a similar ZVI PRB at the Haardkrom site electroplating facility in Kolding, Denmark, was not effective, with speculation being that the TCE present may have depleted the chromium-reducing ability of portions of the barrier (Roehl et al. 2005).

For uranium, a number of conventional ZVI barriers (Bronstein 2005) have been demonstrated, including:

- Bodo Canyon Disposal Site, La Plata County, Colorado—a number of PRBs (composed of ZVI, copper wool, and steel wool) were used to treat arsenic, molybdenum, selenium, uranium, vanadium, and zinc. The barrier containing ZVI operated from August 1999 until June 2004 (when flow ceased from the seep and remediation was no longer needed). It maintained effluent uranium concentrations of less than 0.01 mg/L, and was highly effective in treating contaminants.
- Cotter Corporation Uranium Mill, Cañon City, Colorado—a ZVI PRB was used to treat molybdenum and uranium. Though the barrier eventually failed for molybdenum, uranium concentrations remained at less than 0.006 mg/L. It was found that the ZVI was clogged by mineral precipitants. Modifications, including a pretreatment zone composed of coarse gravel and ZVI, were suggested.
- Fry Canyon Site, Fry Canyon, Utah—a PRB of ZVI, amorphous ferric oxide (AFO), and phosphate rock was used to treat uranium. The ZVI barrier has been the most effective, removing 99.9% of uranium.
- Mecsek Ore Site, Pecs, Hungary—a PRB composed of ZVI and shredded cast iron was used to treat uranium, and concentrations within the groundwater in 2003 were reduced to less than 1% of the influent value after passing through the barrier.

- Monticello Mill Tailings Site, Monticello, Utah—a ZVI PRB was used to treat uranium, arsenic, manganese, molybdenum, selenium, vanadium, and nitrates. Results show that the barrier was effective in treating the contaminants. Nearly all of the uranium, arsenic, manganese, molybdenum, selenium, and vanadium were removed from the groundwater, and nitrate, molybdenum, and manganese were greatly reduced. Since 2000, contaminants have been reduced to below detectable levels.
- Rocky Flats Environmental Technology Site (Solar Ponds Plume), Golden, Colorado—a barrier composed of ZVI and wood chips was used to treat nitrate and uranium. Remediation goals required a reduction of uranium from 20-28 pCi/L to 10 pCi/L. Surface stream samples below 10 pCi/L for uranium indicate that the PRB is working properly.
- Y-12 Site, Oak Ridge, Tennessee—a barrier composed of ZVI and peat materials is being used to treat uranium, technetium, and nitric acid. A funnel and gate barrier failed due to leaking. A continuous trench was subsequently installed and has shown that uranium and technetium concentrations have decreased, but because of reactions with groundwater constituents, the lifespan of the ZVI wall may be significantly shorter than expected.

Overall, these results strongly support the case for using conventional ZVI as an effective reductant for radionuclides, such as uranium. Thus, the potential for iron nanoparticles is considerable. Extensive research is ongoing, including studies on formulation of the iron nanoparticles, delivery vehicles and methods of in-situ stabilization. A potential remedial scheme using ZVI nanoparticles is shown in Figure 2.

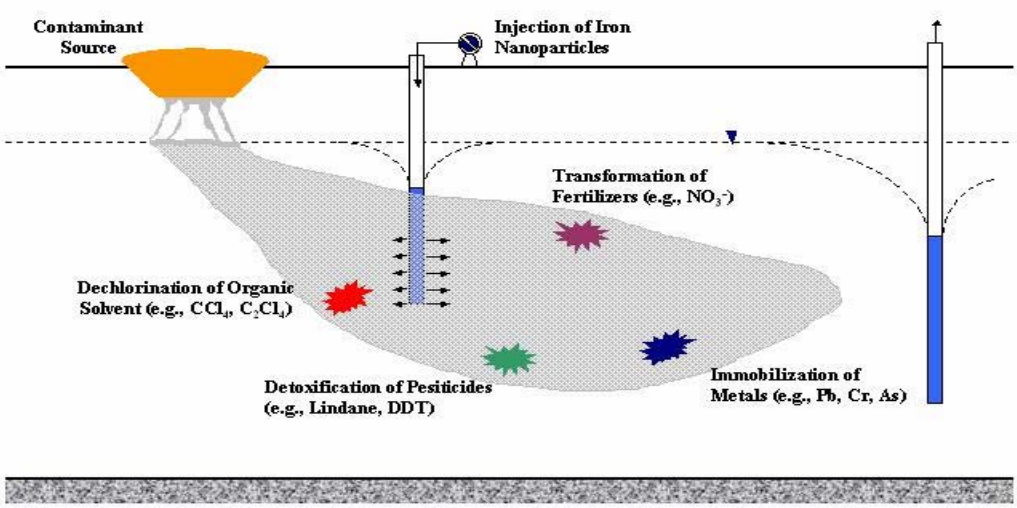

Figure 2. Potential remedial scheme using ZVI nanoparticles

Obviously, a considerable amount of further work must be performed to establish baseline performance and to develop the knowledge base required to gain regulatory

acceptability for the technology as applied to uranium. However, iron nanoparticles remain a leading contender for application to the remediation of radionuclides.

2.2.3 Summary of Environmental Potential

ZVI nanoparticles are the first field application of free-released nanoparticles for environmental remediation. The use of macro-scale ZVI in subsurface PRBs is a well-established technology for the reduction of both chlorinated hydrocarbons and toxic metals in contaminated ground water; ZVI nanoparticles use exactly the same chemistry, but take advantage of the increased surface area and the rheological ability of nanoparticles to flow in the subsurface and permeate crevices where contaminants may reside. The technology is potentially applicable in most circumstances where macro-scale ZVI would be employed. Where mixed contaminants, such as chlorinated organics and higher valency toxic metals, are present, ZVI nanoparticles may be able to accomplish the remediation of both types of material. The demonstrated ability of ZVI to encapsulate a heavy metal contaminant (chromium) through a combination of adsorption and reduction processes, and the ability of ZVI to act as a reducing agent offers significant potential for the remediation of radioactive species such as uranium or plutonium where the reduced form of the metal is of much lower solubility and can be effectively removed from solution. Risk issues are not expected to be significant since data, to date, show that the iron nanoparticles do not travel extensively, and nanoparticles of iron oxides (into which nanoparticulate iron will eventually transform) are ubiquitous in groundwater.

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2.3 Self-Assembled Monolayers on Mesoporous Supports

SAMMS is an award-winning (PNNL 2007) hybrid of two active areas in materials science—mesoporous materials and molecular self-assembly on the mesoporous material surface—that combine to create a material capable of efficiently removing target species from aqueous solutions and other liquids.

A highly developed, engineering-scale technology that is entering the market, SAMMS reached the commercial threshold in 2006 for mercury remediation. The conceptual developer, Pacific Northwest National Laboratory (PNNL) states that currently demonstrated laboratory production capacity is approximately 5 kg. Battelle (the operator of PNNL) and Mobil Oil Corporation (developer of the original mesoporous support, now ExxonMobil) are establishing commercial production capacity for the manufacture of these materials. Mobil has demonstrated the ability to produce mesoporous substrates in batch quantities of one ton or more; scale-up of the functionalization process to these production levels is underway. Costs for these materials are expected to fall into the range of selective anion ion exchange resins. PNNL maintains a Web site devoted to SAMMS. In addition to excellent descriptions of the technology (SAMMS 2006), the Web site provides links to information on:

- current R&D activities;
- publications;
- general articles;
- lanthanide and actinide investigations; and
- Other forms (thiol, chelate, anion, and actinide) of SAMMS.

The following descriptions have drawn heavily from the information contained in the PNNL Web site and its links.

2.3.1 Description

Mesoporous materials, one component of the SAMMS hybrid, are porous substances with pore diameters in the range of 2-50 nm; materials below this size range are called "microporous" (and usually include materials such as zeolites, aluminophosphates (AlPOs), clathrasils, pillared and non-pillared clays) and above this range they are called "macroporous". Mesoporous materials are thus within the 1-100 nm length scale that typically defines nanotechnology. The term "mesoporous" can apply to any material with pore size in the appropriate range, but in the case of the SAMMS technology, structured mesoporous ceramics are usually involved. In 1992, researchers at Mobil, while exploring novel microporous materials for new catalysts, synthesized a new type of silica-based material, named the M41S family, which possessed uniform, mesoporous-scale pores regularly distributed throughout the solid material. The synthesis used cylindrical surfactant micelles to direct (create) the structure formation of the pores in the sol-gel preparation process. The larger pores allow bulk solution to enter and easily explore the interior's entire surface; this is in contrast to the behavior of the smaller pores

typical of zeolites (typically 0.5-1 nm), where size exclusion is often a dominant effect. Fryxell (SAMMS 2006) has described the structure as follows:

> *"To envision what mesoporous ceramic look like, think of a glass honeycomb in which the holes in the honeycomb are very uniform and are only 60 Angstroms across (roughly twice the width of a double-helix strand of DNA), and the walls are only 10 Angstrom thick (about the size of a "typical" amino acid molecule). These parallel, open-ended pores result in a material that has extremely high surface area, all of which is accessible to solution."*

SAMMS are created by attaching a monolayer of molecules to mesoporous ceramic supports. The method uses linear molecules possessing different chemical functionalities at each end. The chemical functionality at one end has an affinity for the mesoporous surface, while the chemical functionality at the other end has an affinity for the target species to be bound by the SAMMS material. A combination of intermolecular and intramolecular forces drive the bi-functional molecules to assemble along the entire length of the pore as a close-packed monolayer, completely covering the surface of the mesoporous support, thus exposing a new chemical surface and interface to bulk solution. Figure 3 (SAMMS 2006) presents a graphical representation of the process.

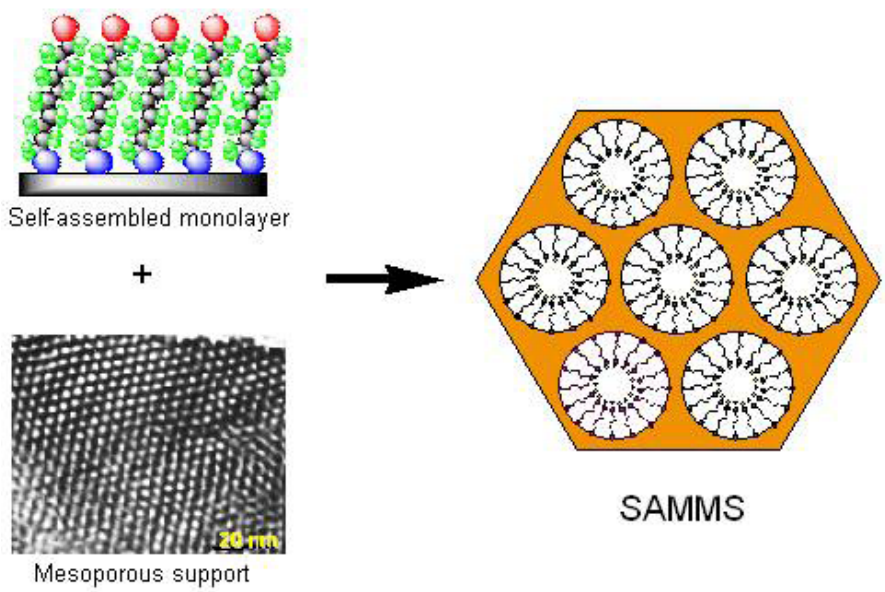

Figure 3. Formation of SAMMS

Possessing physical characteristics similar to activated carbon, mesoporous materials have very high surface area to mass ratios. SAMMS powder can have a specific surface area of approximately 1000 m^2/g. For comparison, the surface of a tennis court is approximately 260 m^2. Monolayer molecules fully cover the available surface and thus present a large area for binding target species. The large surface area, combined with large pore sizes that allow entry of solution, create a hybrid material with fast kinetics, high material loading, and excellent selectivity. Both the properties of the molecules in the monolayer and the pore size of the mesoporous support can be tailored for a specific

application. The functional group facing the interior of the pore can be designed to selectively bind targeted molecules while the pore size, monolayer length, and density can be adjusted to give the material specific diffusive and kinetic properties.

SAMMS is developing in several engineered forms (such as beads, membranes, and membrane cartridges) and can be delivered with a variety of chemically active substances. In addition, the SAMMS technology is developing systematically in a number of functional forms including:

- Thiol-SAMMS, primarily targeting Hg, Ag, Au, Cu, Cd, and Pb;
- Chelate-SAMMS, primarily targeting Cu, Ni, Co, and Zn;
- Anion-SAMMS primarily targeting chromate, arsenate, selenite, and pertechnetate; and
- Actinide-SAMMS primarily targeting Am, Pu, Th, Np, and U.

a. Thiol-SAMMS. Thiol-SAMMS was the first and is the most extensively investigated functional form, having been specifically developed for the removal of mercury from liquid media (Chen et al. 1999, Mattigod et al. 1997). Thiol-SAMMS is also the first commercial application of the SAMMS technology (ChemicalProcessing.com 2006). The Thiol-SAMMS functional form takes advantage of the fact that the thiol functional group has a very strong affinity for mercury (in fact "mercaptans", an alternate name for thiols, derives from the Latin "*mercurium captans*," meaning mercury capturers). In Thiol-SAMMS, a monolayer of mercaptopropyl siloxane coats the mesoporous surface with the thiol groups pointing towards the pore center, presenting a thiol surface to the solution in the lined pores. This surface is able to bind cationic, organic, metallic, and complexed forms of mercury with great affinity (distribution coefficient, or K_d, ~1 x 10^8) and rapid kinetics. A graphical representation is shown in Figure 4.

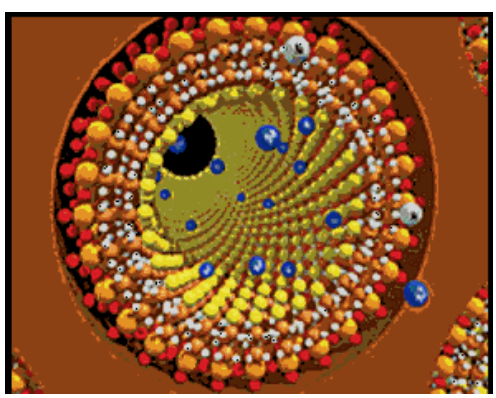

Figure 4. Thiol-SAMMS showing mercury atoms (blue) binding to sulfur atoms (yellow) from thiol groups

b. Chelate-SAMMS. In Chelate-SAMMS (SES 2007, SAMMS 2006), chelating functional groups (such as ethylenediamine, ethylenediamine triacetic acid, pyridine, etc.) are attached to the surface of the mesoporous materials using a similar chemistry

to that used for preparation of the thiol-SAMMS. The chelating group is tailored for the targeted metal (e.g., ethylenediamine for copper and 1,2-hydroxypyridinone (HOPO) for the actinides). Results are promising and research is continuing to optimize the synthesis and metal loadings.

An intriguing aspect of Chelate-SAMMS, and one that demonstrates the versatility of the technology, is through a synthesis modification, which is a functional form of SAMMS that is able to bind cesium (Lin et al. 2001). The basis is that metal ferrocyanides have been widely investigated as ion exchangers for cesium, with potassium cobalt ferrocyanide having the advantages of high capacity and selectivity for cesium, but the drawback of being a very fine powder that is difficult to coax into an effective engineered form. In the SAMMS approach, mesoporous silica is functionalized with an ethylenediamine terminated silane. Copper(II) ions are then incorporated simply by stirring a copper(II) chloride solution with the functionalized mesoporous support for a few hours, and refluxing in toluene to produce Cu-EDA-SAMMS. This is converted to Cu-Ferrocyanide-EDA SAMMS simply by mixing Cu-EDA-SAMMS with sodium ferrocyanide. The conclusion of the work was that:

> *"The synthesis of the cesium selective SAMMS is a simple, direct, and convergent synthesis. These nanocomposite materials are easily made from commercially available bulk materials and are highly selective for cesium from various high-salt and acid solutions. The high surface area of the mesoporous silica creates a high loading capacity for cesium sorption. The fast binding kinetics and high loading capacity of SAMMS sorbent materials are due to the rigidly open pore structure and rapid interfacial chemistry. The chemical specificity results from the selectivity of the copper(II) ferrocyanide interface within the nanoporous structure. This unique combination of properties makes SAMMS-based methodology a strong candidate for the cleanup of cesium-containing nuclear wastes and contaminated groundwater"* (Lin et al. 2001).

<u>c. Anion-SAMMS.</u> Anion-SAMMS functional forms (SAMMS 2006, SES 2007) are being investigated since there is a great need for effective anion binders (e.g., in the cleanup of pertechnetate contamination at DOE sites). While organic ion exchange resins based on quaternary ammonium ion exchange chemistry and inorganic materials, such as alumina, are available, they are orders of magnitude less effective than state-of-the-science cation exchangers. The SAMMS approach mimics the strategy used for Cu-Ferrocyanide-EDA SAMMS by lining the pores of the mesoporous material with cationic transition metals complexes specifically targeting those complexes that would allow for a direct interaction between the cationic receptor and the target anion. Research (Fryxell 2001) has shown that copper or nickel ethylenediamine complexes immobilized on mesoporous silica are extremely efficient ion binding materials for chromate, comparable in terms of loading to the best cation exchangers. By exploiting variations in transition-metal complex chemistry, the promise is held that effective ion exchangers for tetrahedral anions can be developed. It is also worthy of note that Thiol-SAMMS capped with soft metals,

such as silver or mercury, have shown promise as "getters" for radioiodine (Mattigod et al. 2003a, Mattigod et al. 2003b).

d. Actinide-SAMMS. Actinide-SAMMS (Fryxell 2001, Lin et al. 2005, SAMMS 2006, SES 2007) is the least developed area of the SAMMS technology. There exists a body of research on SAMMS applied to lanthanide separations (Fryxell 2001, Fryxell 2004, Yantasee 2005, Lin et al. 2005), and parallels between lanthanide chemistry and actinide chemistry are fairly well understood. In addition, the theoretical basis has been explored (Fryxell 2001) and laboratory experiments suggest that by examining potent actinide binding ligands from prior studies and synthesizing functional forms such as amidophosphonic acid-SAMMS and hydroxypyridinone-SAMMS, excellent actinide sorbents can be developed.

At the present time no studies have been conducted on the fate and transport of SAMMS material.

2.3.2 Operational Considerations

PNNL staff assert that SAMMS is clearly superior to commercially-available sorbents, with 99% of Thiol-SAMMS' mercury-adsorbing action taking place in the first five minutes; tests at PNNL show that the material can remove 99.9% of mercury in a simulated wastewater, reducing the mercury level to well below EPA discharge limits (ChemicalProcessing.com 2006). Treatment costs appear to be an order of magnitude lower than those of the best available alternative technologies.

From ChemicalProcessing.com: "…says Shas Mattigod, a staff scientist at PNNL. 'There is no comparison.' Mattigod calls treatment costs an order of magnitude lower than those of the best available alternative technologies. 'We estimate that it will cost about $200, including material, analysis and labor, to treat similar volumes of this waste solution,' he says. 'This would save $3,200 over the more-traditional disposal methods.'"

2.3.3 Summary of Environmental Potential

The SAMMS technology is one of the most promising nano-enabled environmental technologies. It is probably the only nanotechnology so far that was both specifically designed for, and has already found commercial application in, environmental management. It is a technology used for separating aqueous solutions, but is more likely to find application in sorbent units as opposed to being released into the environment to perform its separatory behavior. Technologically, it combines rational ligand design for targeting species in solution with molecular self assembly on mesoporous support structures. Rational ligand design is well understood; molecular self assembly and mesoporous material behavior are firmly enough understood to allow commercial application. Yet both are benefiting greatly from further developments, many coming from various areas of nanotechnology research. The technology is extremely flexible, allowing a wide variety of aqueous species to be targeted for removal. The SAMMS material offers the benefit of high capacity, and also appears to be a strong candidate as a

waste form that may be disposed of directly, thus significantly easing further processing requirements.

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2.4 Membranes: Nanofiltration and Affinity

2.4.1 Background

The term "membrane" covers a wide range of processes, including those used for gas/gas, gas/liquid, liquid/liquid, gas/solid, and liquid/solid separations. Membrane technology is well-established and is used in many processes. Membrane production is a large-scale operation. Membranes are used for the separation of radionuclides as well as other contaminants. This section discusses three nanotechnologies that are often used in the filtering processes and show great potential for applications in remediation.

1. *Nanofiltration* (and its sibling technologies: reverse osmosis, ultrafiltration, and microfiltration), is a fully-developed, commercially-available membrane technology with a large number of vendors. Nanofiltration relies on the ability of membranes to discriminate between the physical size of particles or species in a mixture or solution and is primarily used for water pre-treatment, treatment, and purification (Van der Bruggen and Vandecasteele 2003, Rautenbach and Groeschl 1990, Rautenbach et al. 1997, Atkinson 2002, Costa and de Pinho 2006). There are approximately 600 companies worldwide offering membrane systems.

2. *Electrospinning* is a process utilized by the nanofiltration process, in which fibers are stretched and elongated down to a diameter of about 10 nm. The modified nanofibers that are produced are particularly useful in the filtration process as an ultra-concentrated filter with a very large surface area. Studies have found that electrospun nanofibers can capture metallic ions and are continually effective through re-filtration.

3. *Surface modified membrane* is a term used for membranes with altered makeup and configuration, though the basic properties of their underlying materials remain intact.

With the global water market valued at over $300 billion, and water supplies becoming an important international issue, nanofiltration is anticipated to have a very important role in the future. In contrast to the types of filtration that rely on size discrimination, affinity membranes use chemical recognition between the components of the membrane and components of solution to effect separation. Affinity membranes and related technologies are well-established and find their primary markets in the biomedical and biotechnology industries.

2.4.2 Nanofiltration Membranes

Nanofiltration is one of a group of similar membrane processes (including reverse osmosis, ultrafiltration, and microfiltration) used to separate components of a liquid mixture. These four processes are best understood together and as a continuum in terms of the size of particles that can be removed from a mixture.

In the regular particle filtration of a liquid containing entrained particles, the liquid mixture is forced (by gravity or applied pressure) through a filter medium that has pores or passages of a size that allows the liquid and small particles to pass through, but prevents passage of larger particles. A paper coffee filter is an example of a regular particle filtration. The paper filter allows passage of the water containing dissolved or extremely small material, but prevents passage of the larger coffee grounds. Smaller pores or passages in the filter medium prevent larger particles from passing through with the liquid. Figure 5 provides a graphical representation of the generalized filtration process.

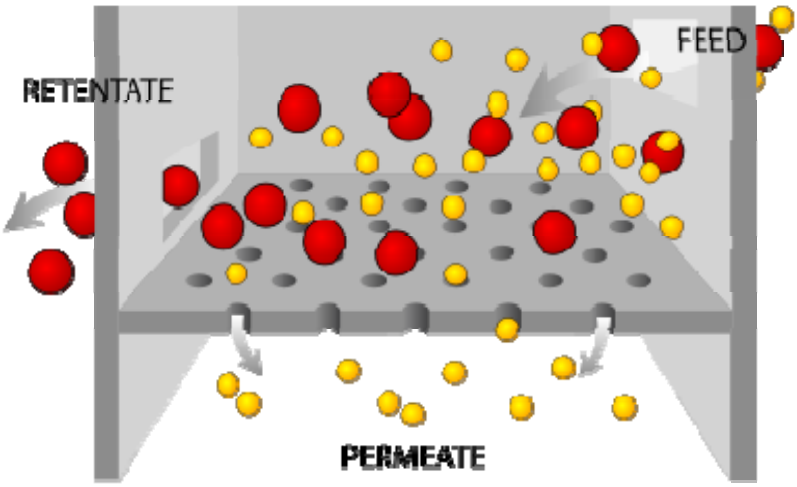

Figure 5. General representation of the filtration process

There are two basic types of filters: depth filters and membrane filters. Depth filters have a significant physical depth and the particles to be retained are captured through out the depth of the filter. Depth filters often have a labyrinthine three-dimensional structure, with multiple channels and heavy branching so that there is a large pathway through which the liquid must flow and by which the filter can retain particles. Depth filters have the advantages of low cost, high throughput, large particle retention capacity, and the ability to retain a variety of particle sizes. However, they can suffer from entrainment of the filter medium, uncertainty regarding effective pore size, some uncertainty regarding the overall integrity of the filter, and the risk of particles being mobilized when the pressure differential across the filter is large.

The second type of filter is the membrane filter, in which depth is not considered important. The membrane filter uses a relatively thin material with a well-defined maximum pore size and the particle retaining effect takes place almost entirely at the surface. Membranes offer the advantage of having well-defined effective pore sizes, can be integrity tested more easily than depth filters, and can achieve more filtration of much smaller particles. They tend to be more expensive than depth filters and usually cannot achieve the throughput of a depth filter. Filtration technology has developed a well-defined terminology that has been well addressed by commercial suppliers; the American Standard Test Method (ASTM) has developed a standard (ASTM D6161-05) (ASTM

2007) that addresses the terminology used for microfiltration, ultrafiltration, nanofiltration, and reverse osmosis membrane processes.

Reverse osmosis, nanofiltration, ultrafiltration, and microfiltration are all membrane processes able to remove small particles or soluble species. They all work on exactly the same principle as regular particle filtration, but the distinguishing feature between them is their effective pore size, and thus, the minimum size of particle that will be rejected by the membrane; reverse osmosis membranes reject all but the very smallest species (small soluble organic species that are not otherwise considered even to be "particles"), while microfiltration allows considerably larger particles to pass through. Figure 6 provides a graphic representation of the process characteristics of the four membrane processes, and Figure 7 provides a graphic representation showing the size range and approximate molecular weight range where each of the four membrane filtration technologies finds its application.

Regular particle filtration will reject particles down to about the one micron (1,000 nm) size range. If filtration to reject particles smaller than this limit is required, microfiltration should first be considered. Microfiltration operates at the low end of familiar particle filtration, being at the limit able to retain particles above the 100 nm size range. Its separating abilities thus cease at the 100 nm limit usually associated with nanotechnology. Microfiltration can remove most suspended solids and living material, such as bacteria, but will not retain any type of dissolved solute or smaller biological material, such as viruses. Ultrafiltration is effective only to the 10 nm size range, allowing it to reject most proteins, viruses, and groundwater colloids. Nanofiltration is usually used to remove material in the 0.5-10 nm range and will reject most of the larger organic molecules, sugars, and multivalent ions, with only monovalent ions and water being able to pass through. To remove the monovalent ions, reverse osmosis membranes are required; these will reject almost all material, except water and simple organic species (such as very short chain alcohols and acids).

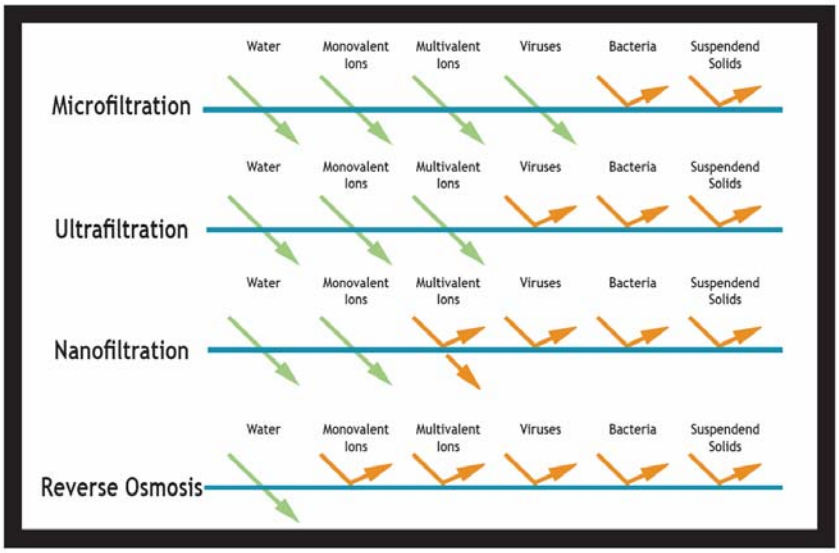

Figure 6. Membrane process characteristics

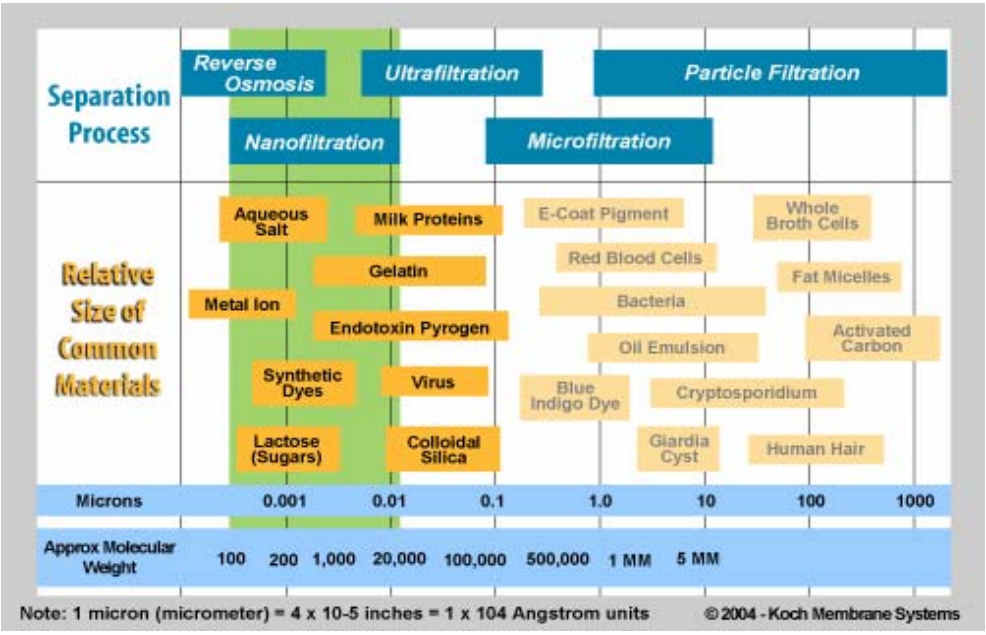

Figure 7. Size range for filtration separation processes

Benefits of water treatment nanofiltration include:

- Lower operating costs,
- Lower energy costs,
- Lower discharge and less wastewater than reverse osmosis,
- Reduction of total dissolved solids (TDS) content of slightly brackish water,
- Reduction of pesticides and VOCs (organic chemicals),
- Reduction of heavy metals,
- Reductions of nitrates and sulfates,
- Reduction color, tannins, and turbidity,
- Hard water softening,
- Being chemical-free (i.e., does not use salts or chemicals), and
- Water pH after nanofiltration is typically non aggressive.

For radionuclide treatment applications, nanofiltration and ultrafiltration have been investigated as an ultra low-level analytical tool to separate actinides from other ionic species in high-level radioactive waste solutions, and as a possible treatment option for waste streams from the Los Alamos National Laboratory Plutonium Treatment Facility (Smith 1993). In these applications, the nanofiltration and ultrafiltration membranes are coupled with water-soluble chelating polymers (WSCP). WSCPs are polymers engineered to contain both highly selective chelating functionalities to bind with targeted metal ions, and solubilizing functionalities to allow the polymer to dissolve in water (Smith et al. 1995). The polymer's overall size is large enough that it exceeds the rejection limit for an ultrafiltration membrane. When the unchelated polymer is introduced into a solution that contains the target ions for which the chelating groups

were designed, the polymer binds with these target ions and nothing else. The chelated polymer can then be separated from the solution (and all other ions in the solution) by ultrafiltration; the chelated target ions can be separated from the polymer by adjusting the solution chemistry; and the regenerated water-soluble chelating polymer can be recycled (Jarvinen 1995). In these applications, ultrafiltration combined with WSCP has the advantage of being aqueous-based (such as ion exchange resins), has a high throughput and rapid kinetics (like two-phase liquid-liquid extraction systems), but does not have the disadvantage of using organic solvent-based extractants.

WSCPs with molecular weights in the 100,000 range have been prepared based on polyacrylic acid or polyethyleneimine with functional groups of phosphonic acid, acylpyrazolone acid, and hydroxamic acid. In acidic nitrate and acidic chloride solutions, these functional groups have a high affinity for actinides and a low affinity for alkali metals and alkaline earths. The concentration of polymer is typically 1-2%, with the ultrafiltration membrane typically having 10-100 µm pores (Gibson 1994, Smith 1993). This technology has been tested at bench scale for the removal of heavy metal ions from electroplating waste streams. Development continues (Moreno-Villoslada and Rivas 2002, Rivas et al. 2003, Rivas et al. 2006, Tomida et al. 1994, Kawano et al. 2002), though dendrimers may compete as a chelating moiety in the future if their costs decrease.

Summary of Environmental Potential

Nanofiltration is an established technology with numerous equipment developers, manufacturers, and vendors. The major application is in reverse osmosis for desalination and production of high purity water for specialized industrial uses, with small applications for wastewater treatment. While current and past development has relied predominantly on size exclusion effects, the promise of nanotechnology is that specific chemical and physical behavior can be engineered into the materials, and that the slow flow rates typical of reverse osmosis and nanofiltration can be overcome—allowing the energy requirements and production costs for the production of pure water to be greatly reduced. The general industrial uses of filtration technology should support developments that will allow spin-off applications for environmental uses; a significant effort is being made to apply nanotechnology developments of filtration technology to the production of potable water in economically challenged arid regions. The primary environmental applications are likely to be “end-of-pipe” and polishing uses. Nanofiltration combined with water-soluble chelating polymers has been investigated for the removal of radioactive species from aqueous waste streams (Smith 1993, Smith et al. 1995).

2.4.4 Electrospun Fibers

Electrospinning is a process for making nanofibers with diameters down to about 10 nm. The technology produces the nanofibers from polymer solutions or melts, with the extreme elongation and narrowing of the fiber occurring as a result of electrostatic repulsion. Electrospinning has the characteristics of both the commercial electrostatic spraying technique and the commercial spinning of fibers, each of which is a long established technology in its own right. Electrostatic spraying is a coating technology,

over a century old, involving atomizing a liquid from a spray gun and imparting an electrical charge to the droplets by using an electrode placed at the end of a spray gun. The electrode typically operates in the 30 to 140 kilovolt range with a current of 0 to 225 microamperes. The droplets are attracted toward a target that is either grounded or has a positive charge, and produces a uniform coating of liquid (frequently paint). The electrostatic spraying approach can also be used as a surface modification technique to introduce nanoparticles onto fibers or other surfaces by spraying solutions that contain only about one particle per droplet.

In comparison, electrospinning (first patented by Antonin Formhals in 1934) uses the electrical charge to form a mass of fine polymer filaments. In electrospinning, a polymer solution or melt is driven through a spray gun nozzle and forms a droplet at the tip. When the voltage is applied to the nozzle, the droplet is stretched; if the viscosity of the material is sufficiently high, the breakup encountered in electrostatic spraying does not occur. Instead, a thin, charged liquid jet is formed. The jet elongates and is whipped continuously by electrostatic repulsion, forcing it to follow a spiral path toward the oppositely charged or grounded collector. The whipping action helps to elongate the jet much further to a diameter on the order of tens of nanometers. Figure 8 illustrates the basic process. Fibers are formed either by the melt cooling or the solvent evaporating from the polymer solution. Nanoparticles can be mixed into, or produced directly in, the polymer solution and spun with the fibers (Lee et al. 2005). Nanofibers produced in this way have many potential applications, including high efficiency filter media, as nanocomposite materials for water treatment membranes, catalysis, hydrogen storage, or in biomedical applications (such as drug release carriers or artificial tissue).

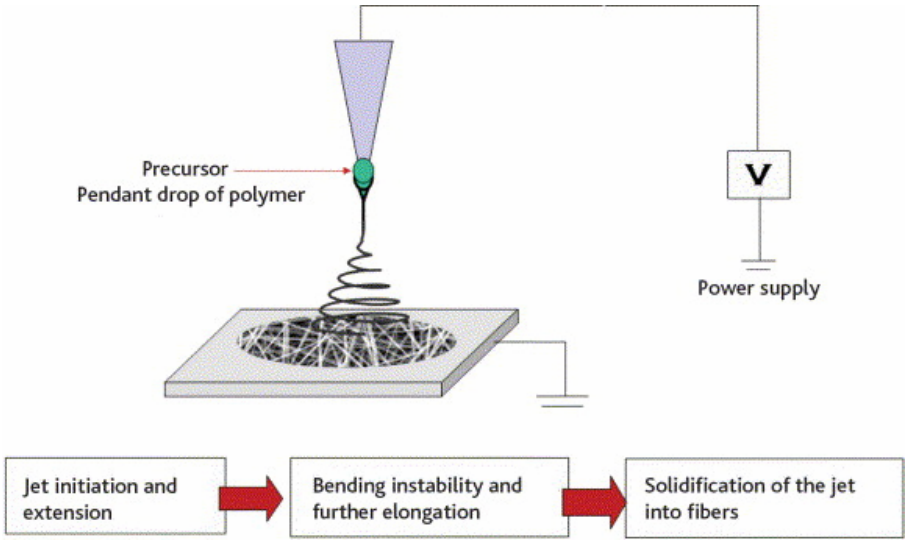

Figure 8. Basic principle of electrospinning

Investigations into the potential of electrospun fibers for water treatment have mainly focused on their use in membranes, where the massive surface area (illustrated in Figure 9) offers special advantages. Ki et al. (Ki et al. 2007) examined membranes of a nanofibrous blend of silk fibroin and wool keratose and found that it had an exceptional performance for the adsorption of metal ions, that its adsorption capacity was maintained after several desorption and re-adsorption cycles, and that it is very suitable for removing and recovering heavy metal ions from water, potentially as an affinity membrane.

Ramakrishna et al. (Ramakrishna et al. 2006) reviewed electrospun nanofibers from the perspective that their porous nature and large surface-to-volume ratio gives them the potential for use in various applications where high porosity is desirable. They noted that electrospinning has an advantage of comparatively low cost with relatively high production rate, that the unique ability to produce nanofibers of different materials in various fibrous assemblies, and that the ability to form porous fibers means that the surface area of the fiber mesh can be increased tremendously. Since the fibers can be surface functionalized, affinity membranes can easily be formed with the potential for application in the removal of heavy metals from wastewater. They concluded that electrospinning may well be one of the most significant nanotechnologies of the 21st century.

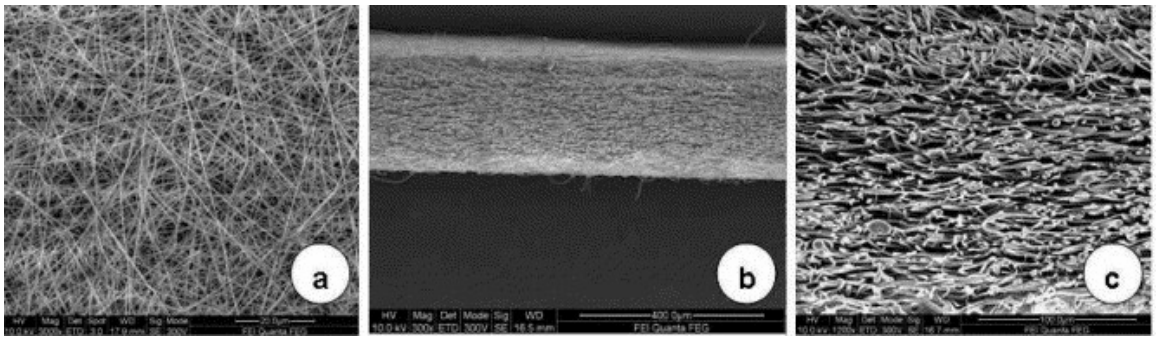

Figure 9. An electrospun polysulphone membrane: (a) surface; (b) cross-section; and (c) magnified cross-section images

Sang et al. (Sang et al. 2008) examined various filtration modes for using an electrospun chloridized polyvinyl chloride nanofiber membrane (including static adsorption, direct filtration, soil-addition filtration, diatomite-addition filtration, and micellar enhanced filtration), and they concluded that the membrane, when used with micellar enhanced filtration, can be used for the treatment of the groundwater containing heavy metals (such as copper, lead, and cadmium) with high efficiency.

2.4.5 Surface Modified Membranes

Electron-beam-induced grafting is one of two methods in the category of ionizing radiation—gamma radiation from cobalt-60 is the other. Electron-beam-induced technology provides a pathway for customizing surfaces such as membranes; hence, the commercial name eMembranes (developed by the Japan Environmental Purification Research Institute). The technology allows membrane surface alternation without

changing the basic properties of the underlying bulk materials. Electron-beam machines are currently available and play a significant role in processing specialty polymeric materials. For example, electron-beam-induced grafting has existed in some form for decades; nuclear power plants have used ion exchange resins enhanced by electron-beam-induced grafting to cleanse uranium from coolants. The future materials generated with this technology is based on over 50 years of scientific research. The technology is stimulating the development of new and promising membranes. Electron-beam-induced grafting is being used by laboratories throughout the world to create surfaces, including chemical resistance, wet ability, biocompatibility, antithrombo, dyability, and antistatic properties. Grafting has also been used to produce ion exchange membranes for the removal of heavy-metal for aqueous waste streams. An emerging application is biological separations, but the basic concept also has targeted the removal of heavy metals from industrial wastewaters. There is little doubt that many new and improved products will be created to aid in the cleanup of radionuclides.

eMembrane technology is being extended to create specialized membranes for many potential applications. The ability to create specialized nano-engineered membranes opens up many envisioned possible future applications. An example of developing applications is a new water remediation technology, which could remove—in one pass—multiple contaminants such as viruses, radionuclides, heavy metals, and chlorinated solvents. A membrane could be tailored for a specific cleanup application. This would greatly reduce remediation costs and accelerate the cleanup process.

The following example of eMembrane development gives an indication of the broad and varied possibilities for developing customized membranes and material surfaces, and draws heavily from company provided literature. eMembrane's technology involves the nano-grafting of polymer chains containing selective binding functionalities. This technology can impart new and multiple polymeric material on existing materials and membranes. At the heart of the technology is the technique of electron-beam induced polymer grafting. Figure 10 provides a graphical representation of the technique showing the attachment of polymeric material.

Figure 10. Electron-beam induced polymer grafting

The polymer chains, or filaments, typically range from 10 nm to 300 μm long. The smallest filaments would catch ions and thus collect toxic metals from water. Larger filaments could hold gas or protein molecules, while the largest could capture whole cells or viruses in a bio-weapon defense system. There are as many as 10 trillion filaments on a square centimeter of substrate, spacing the filaments about 4 nm apart.

An electron beam irradiates a base membrane that can be made from any polymeric material. Other radiation sources, such as gamma rays, can also be used for similar radiation induced polymer grafting (Ramakrishna et al. 2005). The electron beam irradiation generates active species, or radicals, on the surface of the polymer. The active species are the sites at which other long polymer chains or brushes can be attached. The polymer brushes may contain the binding functionalities at the time of attachment, or they may be chemically functionalized after attachment has occurred. Electron beam irradiation is seen as an advantageous method of surface modification since it can occur after the basic polymer has been fabricated and does not affect the shape; by varying the electron beam energy and other process characteristics, the depth and degree of functionalization can be controlled.

eMembrane's electron-beam technology permits a density of polymer brush attachment that is extraordinary—up to 10 trillion polymer brushes per square centimeter can be attached giving a surface spacing of about 4 nm between each brush, a density far exceeding any other technique. The brushes can range from 10 to 300 nm long and can contain a variety of functionalities, allowing the production of highly tailored separation material. For example, a microporous membrane with grafted functionalized polymer brushes not only performs microfiltration (by molecular size cutoff), but the functional groups on its brushes can also simultaneously capture and remove toxic metal ions, soluble proteins, viruses, or cells from the filtrate. In effect, it has become an affinity membrane (Ofsthun et al. 1999, Zou et al. 2001, Nasef 2004, Klein 1991). Materials in a variety of shapes (e.g., film, hollow fiber, non-woven cloth, etc.) are grafted with polymer brushes that extend off the surface of the starting material. Figure 11 provides a graphical representation of the functionalized polymer surface with a variety of brushes attached to facilitate a number of separations.

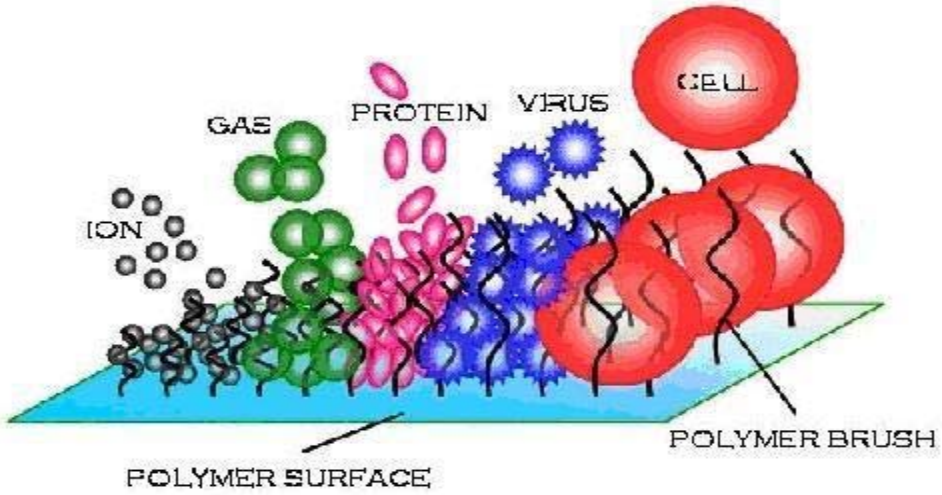

Figure 11. eMembrane-functionalized surface

Environmentally-related applications currently under investigation by eMembrane, Inc. include:

Ion

- Removal, collection of heavy metal ions from fluids,
- Ultra-pure water production
- Immobilized metal affinity membrane

Gas

- Removal of odors or toxic gases via neutralization

Biological

- Tools for proteomics
- Display of multilayer of various proteins for protein-protein interaction studies
- Immobilized enzymes for proteomics, biosensors, and bioreactors
- Large-scale biologics purification

Cell

- Immobilized cells for proteomics studies
- Removal of bacteria
- Bioreactors, artificial organs

Radiation cross-linking of naturally occurring polymers, such as polysaccharides, is being investigated for the production of biodegradable hydrogel/nanogel. This new nanomaterial consists of individual macromolecules that are internally cross-linked by irradiation ionizing radiation.

Specifically modified nanogels are being studied for wastewater filtration. Gels containing acid groups have to bind ions, including uranium and nickel, for use in the removal of metals from aqueous media. These gels can be formulated and customized to remove most contaminants found in water.

No fate and transport studies have been conducted, nor are anticipated, since this is a process unit rather than a material. Because the technology is in the development state, no operational or maintenance parameters have been determined, and no information on impacts, hazards, efficacy, limitations, and waste management approaches is available. One of the greatest, unknown concerns is what could happen if the fibers dislodge from the surface and enter the drinking water supply.

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2.5 Zeolites

2.5.1 Introduction

Zeolites are a well-established technology used in a range of processes and industries. Zeolites are not new materials—they have been investigated for over two and a half centuries, with stilbite and natrolite both being identified in the 1750s. Industrial applications include catalysis in the petroleum industry (Venuto and Dekker 1979, Chen et al. 1994), various uses in agriculture (St. Cloud 2007, BRZ Zeolite 2007, Zeolite Australia 2007), horticulture (ZeoPro 2007), gas separations (Yang 1994, Kerry 2007, Kanellopoulos 2000), domestic water treatment (McKetta 1999, Kawamura 2000, Faust 1998); and nuclear waste processing (Auerback et al. 2003, Choppin and Khankhasayev 1999). The value of zeolite catalysis to petroleum cracking is well in excess of $200 billion (MassNanoTech 2007). About 50 naturally occurring zeolites have been identified; over 150 synthetic zeolites have been prepared and characterized; and further thousands of combinations of framework and composition are available (MassNanoTech 2007, Baerlocher and McCusker 1996). Zeolites have long been used in the nuclear industry (Auerback et al. 2003, Choppin and Khankhasayev 1999) owing to their properties as ion exchangers. The planned siting of the United States' first deep geologic radioactive waste repository at Yucca Mountain in Nevada, where design philosophy called for both engineered and natural barriers (Ahn et al. 1981) to inhibit the transport of any potentially leaking radionuclides, was influenced considerably by the local abundance of the natural zeolites mordenite and clinoptilolite, both of which have large cationic exchange capacities.

2.5.2 Description

Zeolites are crystalline aluminosilicates, compositionally similar to clay minerals, but differing in their well-defined three-dimensional nano- and micro-porous structure. Aluminum, silicon, and oxygen are arranged in a regular structure of $[SiO_4]^-$ and $[AlO_4]^-$ tetrahedral units that form a framework with small pores (also called tunnels, channels, or cavities) of about 0.1-2 nm diameter running through the material. Figure 12 shows a representation of a typical zeolite framework. It should be clearly noted that this is just one of a large and growing number of types of zeolite framework. In 1970, the Atlas of Zeolite Framework Types (Baerlocher and McCusker 1996) listed 27 known frameworks, but by 2003, the number had grown to 145. The variety of size and shape available for the pore structure is the source of zeolites' catalytic activity that is so important to the petrochemical industry.

A second consequence of the framework being built from negatively charged units is that it possesses a net negative charge that must be balanced by the presence of positively charged cations. Most naturally occurring zeolites have the environmentally predominant sodium ion as a loosely bound counter ion. These can be readily displaced by other ions for which a particular framework has a much greater affinity, thus giving zeolites significant ion exchange properties.

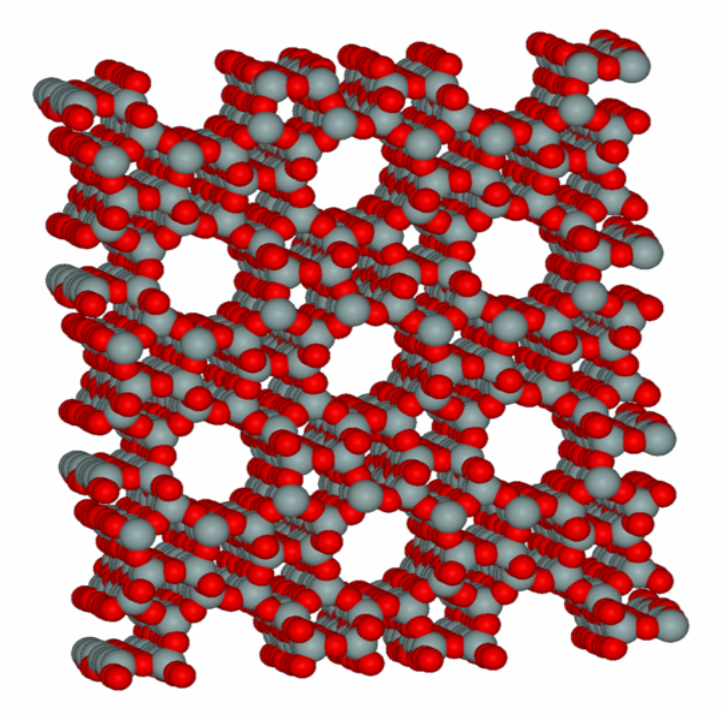

Figure 12. A typical zeolite structure

It should be noted that the ion exchange and the pore size properties of zeolites are partially linked. When the zeolite is in the sodium form (i.e., it has positively charged sodium ions balancing the net negative charge on the aluminosilicate framework), the sodium ions are associated with the tetrahedral aluminum or silicon atoms at the entrance to the pores and, because of their finite size, they effectively reduce the diameter of the pore opening slightly. If the sodium ions are replaced by potassium ions, which are larger than the sodium ions, then the opening of the pore is effectively reduced even further. This behavior permits a degree of control over the size of material that can enter the pores.

Zeolites are usually aluminosilicates, but other tetrahedral atoms such as phosphorus, gallium, germanium, boron, and beryllium can exist in the framework as well.

2.5.3 Potential Applications

General Applications. Zeolites have a wide range of commercial uses (InterSun 2007), including:

Aquaculture
- Ammonia filtration in fish hatcheries
- Biofilter media

Agriculture
- Odor control
- Confined animal environmental control
- Livestock feed additives

Horticulture

- Nurseries, greenhouses
- Floriculture
- Vegetables/herbs
- Foliage
- Tree and shrub transplanting
- Turf grass soil amendment
- Reclamation, revegetation, and landscaping
- Silviculture (forestry, tree plantations)
- Medium for hydroponic growing

Household Products

- Household odor control
- Pet odor control

Industrial Products

- Absorbents for oil and spills
- Gas separations

Environmental Applications. Although environmental applications of zeolites are small compared with applications of their catalytic properties, considerable research and some implementations have taken place including:

Radioactive Waste

- Site remediation/decontamination

Water Treatment

- Water filtration
- Heavy metal removal
- Swimming pools

Wastewater Treatment

- Ammonia removal in municipal sludge/wastewater
- Heavy metal removal
- Septic leach fields

Pasini (Pasini 1996) has described the state-of-the-art technology with regard to the use of natural zeolites in the protection of the environment. He focuses on the possible cation exchange procedures and principles that can be operated at an industrial level; the removal of NH_4^+ from municipal and industrial wastewater; the possibilities for use of natural zeolites for removal of heavy metals from water after laboratory experiments; and how chemical and structural features make zeolites a powerful tool for the decontamination of waters containing radionuclides. The compendium by Misaelides et al. (1999) dealt with general environmental applications and contained much information on the use of zeolites as radionuclide sorbents (Macasek 1999, Bish 1999, Rajec et al. 1999, Colella 1999), including consideration of the sorption and leaching properties of the composites and complexes of natural microporous materials; investigation of natural zeolites and nuclear waste management in the case of Yucca Mountain, Nevada; the sorption of heavy metals and radionuclides on zeolites and clays; and environmental

applications of natural zeolitic materials based on their ion exchange properties. As an example of the depth to which these studies can go, Komarneni (Komarneni 1985) investigated the use of one zeolite, phillipsite, in cesium decontamination and immobilization, citing:

> *"The use of zeolites such as clinoptilolite in nuclear waste decontamination is a common practice (IAEA 1972). Zeolites and zeolitic tufts have also been used to decontaminate low and intermediate-level liquid nuclear wastes (Mercer and Ames 1978) and to separate 37Cs from high-level radioactive defense wastes at Hanford, Washington (Nelson and Mercer 1963, Brandt 1970, Buckingham 1970). Zeolitic ion ex-changers, such as Ionsiv IE-95 (USNRC 1980) which consists of a mixture of natural chabazite and erionite from Bowie, Arizona and Ionsiv IE-96 (which consists of chabazite) + Linde A-51 (Hofstetter and Hitz 1983) are currently used to clean up accident wastewater at the Three Mile Island-Unit II reactor, Middletown, Pennsylvania."*

Radionuclide Applications. Zeolites are one of the few nanotechnologies that have been investigated for environmental remediation purposes. Because of their ion exchange properties, and the fact that they are a seemingly benign natural product that can bring certain improvements (such as increasing the soil cation-exchange capacity and soil moisture, improving hydraulic conductivity, increasing yields in acidified soils, and reducing plant uptake of metal contaminants) to soil properties (Allen and Ming 1995), zeolites have been examined for their ability to remediate heavy metals in soil (Weber et al. 1984). Based on this work, Campbell and Davies (Campbell and Davies 1997) performed an experimental investigation of plant uptake of cesium from soils amended with clinoptilolite and calcium carbonate.

The origin of this work was the observation that radioactive cesium (^{137}Cs) from the Chernobyl accident of 1986 has unexpectedly remained in a bioavailable form in upland, sheep-grazing soils of Great Britain. As a potential remedial measure, the zeolite clinoptilolite was tested in a greenhouse pot experiment for its effectiveness in selectively taking up cesium from two British soils: a lowland loam and an upland peat. Rye-grass grown on 10% clinoptilolite-treated soils resulted in grass leaf tissue cesium concentrations below 30 mg Cs kg^{-1} grass in all cases. Where no clinoptilolite had been added, cesium in grass leaf-tissue reached 1,860 mg kg^{-1} in rye grown on peat and 150 mg kg^{-1} in rye grown on loam. In contrast, the addition of calcium carbonate to the Cs-treated, clinoptilolite-free peat soil enhanced the grass concentration of Cs by approximately five times, but this effect was not observed with the concentration of Cs in grass grown from loam soils with the same treatments.

However, despite this apparent beneficial result of adding the zeolite, adverse side effects were observed. Since the zeolite is in the sodium form, sodium ions are released and the risk of sodium toxicity to plants increases as cation exchange proceeds. Further, since clinoptilolite binds heavy metals in general, essential heavy metals (such as zinc) would be markedly decreased by the application of zeolite, which in turn could result in deficiency problems in animals. It was also noted that since grazing animals consume a

considerable amount of soil in their diet, the consumption of radionuclide-laden zeolites could itself bring risks.

In general, it has been noted that the main research behind the use of natural zeolites as a remediation tool for contaminated soil has been conducted largely through laboratory and greenhouse trials. There is very little evidence in the literature to support the long-term use of natural zeolites in real remediation projects (Stead et al. 2000). It was also noted that the future potential of using zeolites has not been fully appreciated, and that there is an urgent need to undertake field trials and evaluate the in-situ efficiency for these remediation purposes.

Since zeolites are natural materials and are mainly used in industrial processes, little research is focused on their fate and transport, though an extensive volume of work exists on their geological origin and behavior. Extensive data exists on operation and maintenance parameters. As would be expected, specific details are highly dependent on waste streams involved. Three references (IAEA 1967, IAEA 1984, IAEA 2002) discussed below provide an excellent overview of the issues involved.

2.5.4 Impacts, Hazards, Efficacy, and Limitations

Zeolites are a bulk commodity. World production is on the order of 4 million tons per year, with China producing and using about 2.5 million tons (primarily as a low-grade additive to pozzolan cement); U.S. consumption is about 0.5 million tons. The primary industrial use is as a petrochemical catalyst and the second largest use is as a detergent builder. Thus, the use of zeolites in radionuclide remediation would be expected to have little impact. Most zeolites, particularly those with current widespread uses, are regarded as a safe material; they are currently being marketed as a health food and references to their medicinal use date back thousands of years. Zeolites are also used as a feed additive for cattle, pigs, chicken, and fish. It should be noted, however, that one zeolite, erionite, is regarded as a carcinogen due to its fibrous nature and high iron content.

Regarding efficacy, though zeolites have had limited uses in environmental remediation outside of their use in the nuclear industry as an ion exchanger for liquid radioactive waste management, they are seen as having significant potential. Even the drawbacks mentioned in the work of Campbell and Davies (Campbell and Davies 1997) (discussed in Section 2.5.3) should be surmountable. To eliminate the sodium toxicity risk to soil, the zeolite could be preconditioned into the ammonium form, which would likely lead to plant growth improvements. Overcoming the concern of nutritionally important soil nutrients binding together would require that the zeolite used (possibly synthetic) would be designed to have a very high specificity for the target radionuclide and little else. Alternatively, soil quality could easily be monitored and appropriate amendments made.

2.5.5 Management of Zeolite Wastes

Ion exchange in general is one of the most well-developed, common, and effective treatment methods for liquid radioactive waste, and is widely used in the nuclear industry. Zeolites are a large component of the inorganic ion exchangers used and an

extensive amount of literature exists on various aspects of their treatment and disposal. Among the best overviews of this technology base are the series of technical reports issued by the International Atomic Energy Agency (IAEA) in 1967, 1984 and 2002 (IAEA 1967, IAEA 1984, IAEA 2002). The information below draws largely from the most recent of these reports (IAEA 2002).

Prior to treatment for disposal, two pre-treatments—dewatering and size reduction—may be needed. Dewatering is generally accomplished by pressure, vacuum filtration, or centrifugation. If drying is needed, hot air is usually used as the drying medium with a shallow bed of spent materials. Types of drying units include fluidized bed dryers, vertical thin film dryers, and cone dryers.

Since inorganic ion exchange materials (such as zeolites) are generally resistant to degradation by radiation or biological actions, they are treated by the use of direct immobilization, or by high temperature processes (such as vitrification). The immobilization matrices currently used include vitrification, cement, bitumen encapsulation, polymer encapsulation, and disposal in high-integrity containers.

Vitrification has been widely evaluated for the immobilization of highly-active waste, such as waste from the reprocessing of spent nuclear fuel, and has been evaluated for the treatment of ion exchange resins (Jantzen et al. 1995, Cicero-Herman et al. 1998). The excellent leach resistance property of the resulting glass waste form is the principal advantage of vitrification. Vitrification processes are capital-intensive, and the melters have a relatively short operational life (approximately 5 years). Vitrification processes operate at temperatures ranging from 1100°C to 3000°C, depending on the waste composition and glass forming additives used.

Cement immobilizing radioactive waste has been used in the nuclear industry and at nuclear research centers for more than 40 years. Detailed descriptions of the process can be found in references from the IAEA in 1993 and the Los Alamos National Laboratory in 1997. Cement has many characteristics in its favor: it is readily available and widely used in civil engineering, the raw material is inexpensive, and the processing equipment can be based on conventional technology. The resulting waste forms are strong; noncombustible and radiation resistant, have a high density (providing radiation shielding), have a reasonable chemical stability, and have a moderate resistance to the release of radionuclides. The high pH conditions typical for cement results in a low solubility for many radionuclides by the formation of hydrolyzed species, carbonates, etc., which provides a good resistance to leaching. The main disadvantage of the cementation of spent ion exchange materials is that the final waste volume is high compared with the initial volume, owing to the low waste loadings that are achievable. The loadings can be increased by a pretreatment (such as grinding) of the spent ion exchange materials before cementation, which improves the quality of the final cemented products.

Bitumen is a generic term used to cover a wide range of high molecular weight Hydrocarbons. Bitumen encapsulation is currently not used in the United States for

disposal, although several bitumen varieties are commercially available overseas for the immobilization of radioactive waste, including spent ion exchange resins. The main characteristics that make bitumen suitable as a matrix material are:

- Its insolubility in water;
- Its high resistance to the diffusion of water;
- Its chemical inertness;
- Its plasticity and good rheological properties;
- Its good aging characteristics;
- Its high incorporation capacity, which leads to high volume reduction factors; and
- Its instant availability at a reasonable cost.

However, since it is an organic material, bitumen has the following disadvantages:

- It decreases in viscosity as a function of temperature, leading to a softening of the matrix, which melts at temperatures of about 70°C;
- It is combustible, although not easily flammable (the flash point and flammability temperatures are higher than 290°C to 350°C, depending on the type of bitumen);
- It has a lower stability against radiation than cement, especially under the higher radiation fields often associated with spent ion exchange media; and
- It reacts with oxidizing materials such as sodium nitrate.

The immobilization of spent ion exchange resins in polymers is practiced at many installations worldwide. Different types of polymers are used and further studies to improve cost effectiveness, process simplicity, and product quality are being carried out in many countries. Among the many polymers used are epoxy resins, polyesters, polyethylene, polystyrene and copolymers, urea formaldehyde, polyurethane, phenol-formaldehyde, and polystyrene.

2.5.6 Summary of Environmental Potential

Zeolites are a well-established technology with a variety of industrial uses ranging from construction materials and detergent builders, to catalysts and separation agents. They are one of the oldest separation technologies for the removal of radioactive components from aqueous waste streams. The flexible tectonic structure and ability to be chemically "tailored" to specific target species continues to stimulate their development. In addition to their use as an "end-of-pipe" treatment for aqueous streams, zeolites are one of the few materials offering the possibility of being an inexpensive amendment to soils contaminated with radioactive species, since extremely high species selectivity and binding strength can be designed into the material. Continued investigation of zeolites in general is expected due to their catalytic properties; research in this area should support further developments, potentially leading to environmental applications.

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2.6 Other Nanoparticles

Though iron nanoparticles presented in Section 2.2 are the most fully developed type of nanoparticle for environmental remediation, they are not the only type of nanoparticle that has been suggested for environmental remediation. Some additional possibilities include the use of TiO_2 nanoparticles as photocatalysts for the destruction of organic pollutants (Rajh et al. 2003), the separation of ionic solutes using nanoparticle-crosslinked polymer hydrogels (Thomas et al. 2003), or the use of coated magnetic nanoparticles in high-gradient magnetic separations (Moeser et al. 2004). The subsections below present information on three possibilities: nanodiamonds, dendrimers, and Argonne Supergel.

Nanodiamonds are the subject of much research due to their potential in electronic and bio-imaging applications, and because they can be prepared directly, simply, and in potentially large amounts. They are apparently biologically benign, and their ease of surface functionalization and magnetic properties make them a potential separation platform.

Dendrimers are a new class of polymer with tailorable properties, both at the surface and in the interior of the particle. They have been of great interest in the area of separations, and are potential complements to separation processes involving nanofiltration or microfiltration.

Argonne Supergel is presented as a nano-enabled technology developed specifically for radionuclide decontamination. These three examples (nanodiamonds, dendrimers, and Supergel) are presented to provide a sense of the range of possibilities that nanoparticles can offer for separation-based remediation.

2.6.1 Nanodiamonds

Nanodiamond is a term used for a group of diamond-related materials with nanoscale dimensions, including diamond films and diamond nanoparticles. These are prepared by a variety of methods, including high-pressure gas-phase nucleation and application of shock waves to graphite (Dolmatov 2001). Within this group of diamond materials lies a subgroup called detonation Nanodiamond (DND), or ultrananocrystalline diamond (UNCD). These materials were discovered in Russia in 1963, and produced by the detonation of oxygen deficient explosives, such as a 3-to-2 mixture of 2,4,6-Trinitrotoluene (TNT) and Hexahydro-Trinitro-Triazine (RDX). Figure 13 shows a Transmission Electron Microscope (TEM) image of DNDs.

DNDs were unknown in the West until recently, and have attracted much interest (Petrov et al. 2006, Gruen et al. 2005) because of their unusually uniform shape and size distribution and the fact that they can be produced in large quantities (Osawa 2003). Before DND was widely known, Western industry produced microdiamonds by applying an externally produced shockwave to heated graphite at high pressures. This produced a polycrystalline material with a wide size distribution and very few particles reaching

down to the 10-20 nm size range. In contrast, DND has a fairly tight size distribution in the 3-5 nm range, consisting of about 5,000 carbon atoms, and has a regular octahedral shape (Figure 14).

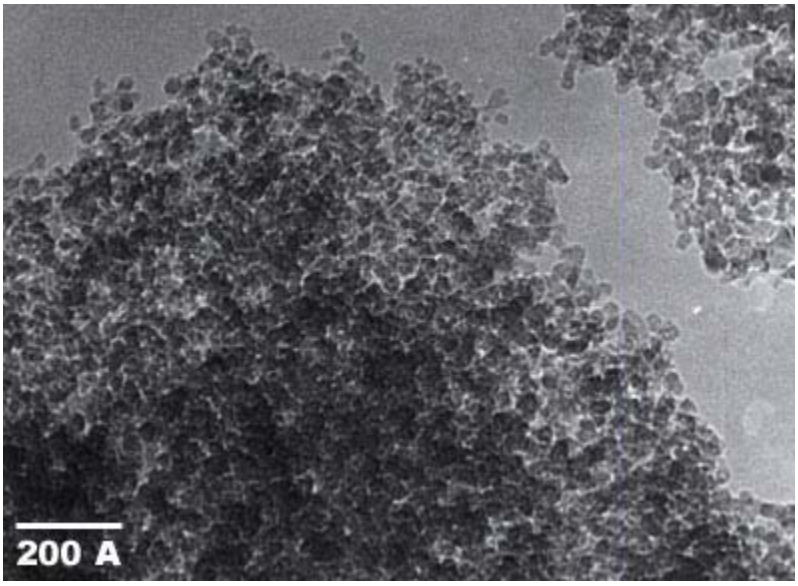

Figure 13. TEM image of DND

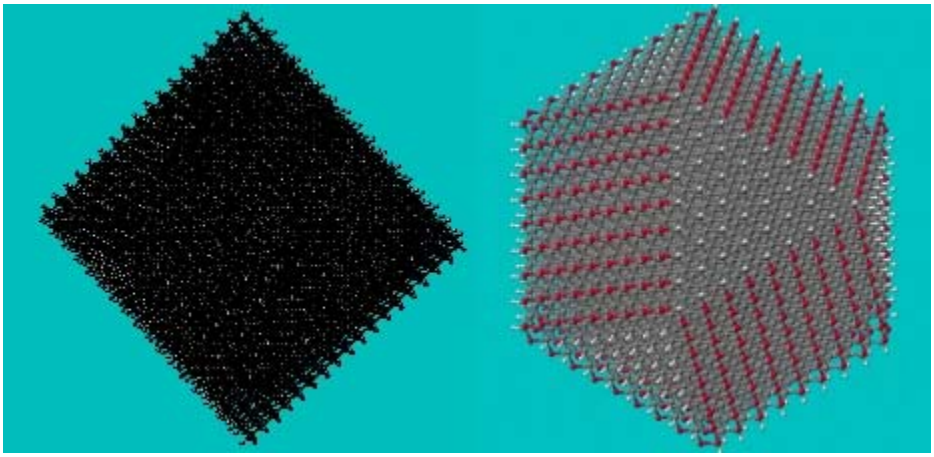

Figure 14. Model of nanodiamonds demonstrating their regular octahedral shape

Nanodiamond production from a detonation produces a sooty product that is approximately 50% DND. To obtain the nanodiamonds from this mixture, two challenges must be overcome—the presence of graphitic impurities and the fact that the diamonds tend to aggregate into clusters with average sizes of 30 μm, 3 μm, and 100-200 nm. The aggregates can be broken up by a combination of ultrasound and high-speed zirconia bead milling.

Nanodiamonds possess interesting properties. Their surfaces have a tendency to change from the regular diamond structure to a fullerene (buckyball) structure (Figure 15), resulting in a material that appears to have a diamond within a fullerene cage and has some of the physical properties of the nanodiamond combined with the rich chemistry of the fullerene.

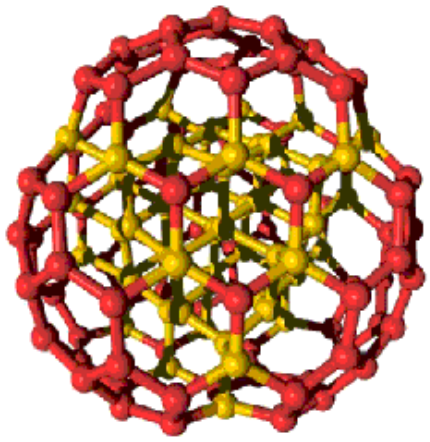

Figure 15. Structure with nanodiamond center and fullerene-like surface

The potential for surface chemical functionalization opens up a wide range of possible applications for derivatized material. Even without chemical functionalization, nanodiamonds have been suggested for a range of applications, including:

- Lapping and polishing applications
- All-rigid memory disk substrate
- Polycarbonate and CR-39 eyeglass lenses
- Miniature and precision ball bearings
- Optical and laser optical components
- Ceramics
- Precious stones
- Metallic mirrors and precision metal polishing
- Ferrite surface preparation
- Mechanical seal lapping
- Superhard and soft nanoabrasives

Other applications include:

- Surface germination for following growth of diamond-like films
- Ni-Diamond and Cr-Diamond electroplated hard coatings
- Molecular sieves
- Lubricant additive to engine oil
- Dry lubricants for metal industry (drawing of W-, Mo-, V-, Rh-wires)
- Reinforcing fillers for plastics and rubbers
- Chromatographic carriers

A major area that is being investigated is the biomedical potential of nanodiamonds, including their roles as drug carriers, implant coatings, and medical nanorobots. Nanodiamonds are soluble in water, can be functionalized, and appear to be biologically benign. Cytotoxicity research findings from the University of Dayton indicate that nanodiamonds are biologically compatible materials across a range of sizes with regard to a variety of cell types, with or without surface modifications (Schrand et al. 2007).

Nanodiamonds have also been suggested as sorbent materials (Dolmatov 2001, Gruen et al. 2005), giving rise to the possibility of environmental remediation applications. Their observed magnetic properties (Talapatra 2005) also open the possibility of their use in magnetic separations. The radiation stability of the carbon also opens up the possibility as a disposal waste form.

2.6.2 Dendrimers

A dendrimer is a highly and repetitively branched, three-dimensional polymer created by a sequence of iterative chemical reactions starting from a central core. Each iteration is known as a generation and has twice the complexity of the prior generation. The term comes from *dendron* (the Greek word for tree), with the analogy being the branch-like structure of the dendrimer. Dendrimers have been called the fourth major class of polymeric architecture (after linear, cross-linked, and branched polymers), but unlike other polymers where atom-by-atom control is not feasible and polydispersity (and the variability it brings) is an inherent characteristic, dendrimers are characterized by monodispersity (i.e., all dendrimer molecules are of a uniform and controllable size) and well-defined properties. Figure 16 provides a graphical representation of a generalized dendrimer structure.

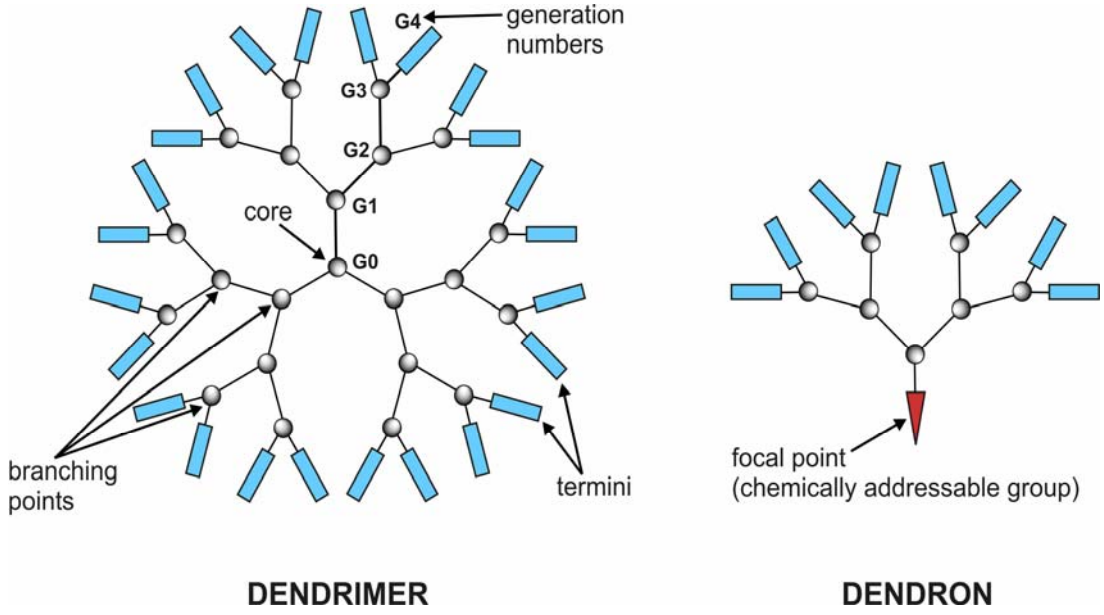

Figure 16. A generalized dendrimer structure

Figure 16 allows some of the special chemical properties of dendrimers to be explained. Starting at the core (G0) and moving through branching points G1 and G2, it can be seen that as the dendrimer branches out in a predictable manner, large voids can exist within the dendrimer internal structure. Both the size and the physical nature (e.g., hydrophobic or hydrophilic characteristics) of these voids can be controlled during synthesis by judicious selection of both the length and composition of the branch backbone. These voids can be used to store material (metals, organic and inorganic molecules, and even other nanoparticles), and together with the fact that dendrimers can easily move across biological membranes, the controllable nature of the voids has led to suggested applications of dendrimers as carriers of genetic material into cells (Kukowska-Latallo et al. 1996), drug delivery agents (Lim and Simanek 2005), and diagnostic imaging agents (Tomalia 2003). The voids can also be used to hold material undergoing reactions and has led to investigations of dendrimers as nanoreactors (Chung and Rhee 2003).

A second feature that is illustrated in Figure 16 is the surface formed by the terminal groups. As the number of generations of the dendrimer increases, the total external surface area rises dramatically. If the terminal groups are designed to be binding moieties for other species, then it is apparent that a dendrimer, compared to say a macroscopic bead of ion exchange resin (which will have a much smaller surface area than an equivalent amount of dendrimer), can potentially bind up a large amount of target material. It is this aspect of dendrimers that is of prime concern for environmental applications. Current expertise in dendrimer synthesis also allows for more than one type of terminal group to be attached to the dendrimer, thus offering the possibility of multifunctional molecules. Terminal groups can be attached to modify solubility, modify binding capacity and specificity, and to allow further reaction with or attachment to other surfaces or nanoparticles. It has been suggested that amphipathic dendrimers could be synthesized with one half of the molecule (or one hemisphere) covered in hydrophobic groups, and the other half containing hydrophilic groups.

Due to the degree of structural control that dendrimers make possible, and the fact that their highly customizable properties should make them building blocks for other nanomaterials, they have been the subject of much research, with the number of academic publications approaching ten thousand. Commercial development has been slower than once anticipated because of their high cost (on the order of $10 per milligram) and the complexity of scaling-up production. Though these factors are themselves subject of much research, dendrimers already have a market or near-market presence:

- Dade Behring, one of the world's largest medical diagnostic firms, is developing a dendrimer-based, rapidly responding tool for detecting heart attacks and cardiac damage.
- The U.S. Army Research Laboratory is developing a dendrimer-based anthrax detection agent.
- Starpharma is developing the world's first dendrimer-based drug, Vivagel, to fight sexually transmitted infections. It has been awarded $20 million by the National Institutes of Health (NIH) to develop its HIV indication; given further awards to

develop its genital herpes indication; and was granted Fast Track status by the U.S. FDA in 2006 as a product for preventing HIV infection.

Dendrimers are currently under investigation as metal sequestering agents for waste remediation technologies (Cohen et al. 2001), and for the removal of uranium from aqueous streams (Diallo 2007). In the latter work, dendrimers may be compared with chelating agents, which are widely used in uranium separation processes, such as solvent extraction or ion exchange resins. Ion exchange resins with amino groups typically bind on the order of 100 mg of uranium per gram of resin, while the work with poly(amidoamine) and poly(propyleneimime) dendrimers, which contain nitrogen and oxygen donors, can bind up to 2500 mg of uranium per gram of dendrimer without reaching saturation in either acid or basic solutions. Further, the binding kinetics of the dendrimers to uranium is very fast and reaches equilibrium in less than 20 minutes. Rapid equilibration, high loading capacity, and selectivity mean that such dendrimers could thus serve as high capacity and selective chelating agents for uranium. The dendrimer-uranium complexes could be easily separated by ultrafiltration and then regenerated, thus avoiding the need to add further reagents and simplifying the overall process.

2.6.3 Argonne Supergel

Argonne National Laboratory (ANL) has developed a system, called the "Supergel" technique, to safely capture and dispose of radioactive elements in porous structures outdoors (such as buildings and monuments), using a spray-on, super-absorbent gel and engineered nanoparticles (ANL 2006). Porous structures are notoriously hard to clean. In decommissioning and decontamination operations, it is common practice to demolish contaminated structures or completely remove a significant surface layer rather than attempt to remove radioactivity. ANL's Supergel technique preserves surfaces, which means that monuments or buildings would not have to be defaced to remove radiation. The Supergel was developed with funding from the Department of Homeland Security to help fill a technology gap in preparedness for a terrorist attack with a "dirty bomb" or other radioactive dispersal device, but it could also be used in more general decontamination situations.

The Supergel technique uses commercially available equipment in a simple procedure. First, a wetting agent and a super-absorbent gel are sprayed onto the contaminated surface. The polymer gel used to absorb the radioactivity is similar to the absorbent material found in disposable diapers. When exposed to water, the polymers form something similar to a structural scaffold that allows the gel to absorb a large amount of liquid. When sprayed on concrete, the wetting agent causes the bound radioactivity to re-suspend in the concrete pores and the superabsorbent polymer gel then draws the liquid out, along with the resuspended radioactivity. Inside the gel, the radioactive material becomes fixed by engineered nanoparticles that also reside in the gel. After a period of standing, the gel is vacuumed and recycled, leaving behind a relatively small amount of radioactive waste for disposal.

2.6.4 Summary of Environmental Potential

These three technologies—nanodiamonds, dendrimers, and Supergel—demonstrate the broad potential of nanoparticles. Nanodiamonds, though relatively new, offer a wide range of potential applications and can be produced in bulk at reasonable prices. Dendrimers are a new class of polymer architecture that has caused much excitement due to the potential of engineering properties at the molecular level into materials of uniform and controllable size. The Argonne Supergel shows the ease with which nanoparticles can be incorporated into other applications to address highly specific technology needs.

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2.7 Uranium Reduction by Bacteria

Bioreductive immobilization of uranium is a quasi nanotechnology. The precipitated uranium and other minerals are in the form of nano size particles, whereas the bacteria are about 1 μm. In this section, the process is described, equations are provided, and photographs presented showing the nanoscale uraninite particles.

The large number of contaminated sites and volumes of contaminated groundwater and soil call for innovative and economically attractive remediation technologies. To date, pump-and-treat is the most widely used technology. Frequently, pump-and-treat has been ineffective in permanently lowering contaminant concentrations in groundwater (Travis and Doty 1990). A recent study by Quinton et al. (Quinton et al. 1997) showed that groundwater cleanup technologies (such as pump and treat, permeable reactive barriers with ZVI, and bio-barriers) are more expensive than in-situ bioremediation.

Microorganisms can reduce uranium indirectly by producing hydrogen sulfide (H_2S) or pure hydrogen (H_2) in the course of other processes (abiotic reduction) or directly using enzymes (enzymatic reduction). The first microorganisms identified to enzymatically reduce U(VI) were the dissimilatory Fe(III)-reducing microorganisms, *Geobacter metallireducens* and *Shewanella putrefaciens* (Lovley et al. 1991). These microorganisms used uranium as an electron acceptor, H_2 or acetate as an electron donor to support growth, and tolerated U(VI) concentrations as high as 8 mM. Several authors studied the enzymatic reduction of U(VI) by various pure or mixed cultures of microorganisms, including metal- and sulfate-reducing bacteria (a summary of previous work can be found in Abdelouas et al. 1999a). These authors reviewed the literature on microbial reduction of uranium and the significance of biogeochemical processes related to uranium mining, tailings, and groundwater remediation. In Figure 17, the key reductive and oxidative reactions are shown for this process; in Figure 18, a bacterium is shown surrounded by nanosize uraninite particles.

$$1/4\ O_2(g) + H^+ + e \longrightarrow 1/2\ H_2O$$

$$1/5\ NO_3^- + 6/5\ H^+ + e \longrightarrow 1/10\ N_2\ (g) + 3/5\ H_2O$$

$$1/2\ MnO_2 + 1/2\ HCO_3^- + 3/2H^+ + e \longrightarrow 1/2\ MnCO_3(s) + H_2O$$

$$1/2\ UO_2(CO_3)_2^{2-} + H^+ + e \longrightarrow 1/2\ UO_2(s) + HCO_3^-$$

$$FeOOH(s) + HCO_3^- + 2\ H^+ + e \longrightarrow FeCO_3(s) + 2\ H_2O$$

$$1/8\ SO_4^{2-} + 9/8\ H^+ + e \longrightarrow 1/8\ HS^- + 1/2\ H_2O$$

- Oxidation of ethanol

$$1/5\ C_2H_5OH + 1/4\ H_2O \longrightarrow 1/6\ CO_2 + H^+ + e$$

Decreasing redox intensity

Figure 17. Reductive and oxidative reactions

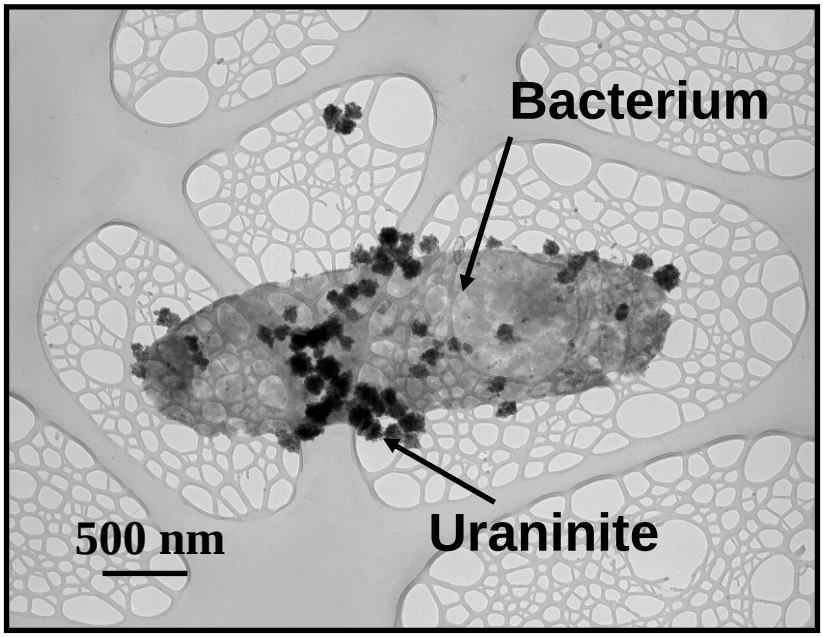

Figure 18. Microphotographs showing a bacterium surrounded with uraninite nanoparticles

The first demonstration of a feasible process for the in-situ immobilization of uranium as a bioremediation strategy was conducted by a team of scientists from the University of Massachusetts, PNNL, the University of Tennessee, and several other institutions (Anderson 2003). The team conducted a two-month field study and demonstrated that by adding acetate to the subsurface, they could stimulate the growth and proportion of *Geobacter* species within the subsurface microbial community. At the same time, the concentration of uranium in the ground water was greatly reduced.

The observation of bacteria able to immobilize uranium is an area of active study, both from biochemical and nano-geological perspectives. Comparatively little is known about either the bacteria or the processes they use; even questions over the long-term stability of the immobilized uranium have yet to achieve a comprehensive answer. Recent research at Virginia Polytechnic Institute (Virginia Tech 2006) with *Shewanella oneidensis* MR-1 (one of the most common bacteria in the Earth) has shown that particle size is important, with smaller nanoparticles of the iron (III) oxide hematitie showing a lower rate of reduction than larger nanoparticles. Research on the same bacterium at PNNL (Marshall 2006) has demonstrated that much of *Shewanella*'s biochemistry of immobilization occurs outside the cell, producing uniform, 5-nm particles of uraninite trapped as strings of particles in a glue-like extracellular polymeric substance (Figure 19).

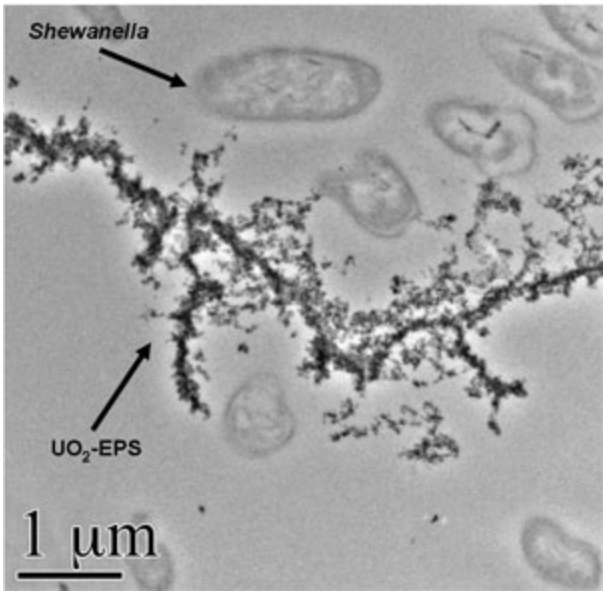

Figure 19. Uraninite nanoparticles trapped in an extracellular polymeric substance exuded by *Shewanella*

A current five-year, $15-million U.S. Department of Energy (DOE) project led by Oak Ridge National Laboratory (ORNL) (Edwards 2007) is trying to provide a further understanding of the coupled microbiological and geochemical processes limiting radionuclide bioremediation, and through an examination of terminal-electron accepting processes involving *geobacteraceae* has shown that due to the stress imposed by low pH on microbial metabolism, the terminal-electron accepting processes of acidic subsurface sediment are inherently different from those of neutral pH environments and

neutralization will be necessary to achieve sufficient metabolic rates for radionuclide remediation.

In addition to direct bacterial processes for the reduction of uranium, indirect processes may occur where bacteria or other microbes assist in the reduction processes by control of the chemical environment. The dissimilatory iron reducing bacteria mentioned above metabolically couple the oxidation of organic compounds with the reduction of Fe (III) generating energy and Fe(II) complexes, the latter of which in turn lead to the production of a range of Fe(II) minerals such as magnetite, siderite, vivianite, ferruginous smectite, and green rust. In fact, the oxidation/reduction behavior of uranium, together with the ability of micro-organisms to take advantage of such oxidation/reduction behavior, may well play a significant role in the formation of uranium ore deposits (Dexter-Dyer 1984). This behavior is being exploited in the concept of microbial mining of uranium, and may be of importance to remediation. An example is "green rust", a class of iron (II)/iron (III) hydroxide compounds having a pyroaurite-type structure consisting of alternating positively charged hydroxide layers and hydrated anion layers. Green rusts are products of both abiotic and microbially induced corrosion of iron, and occur in both microbially mediated and abiotic reductive dissolution of ferric oxyhydroxides. Extended X-Ray Absorption Fine Structure (EXAFS) studies have shown that uranyl ion can be reduced to UO_2 (U(IV)) by green rust (O'Loughlin 2003), with the uraninite forming nanoparticles on the green rust crystal surface (Figure 20).

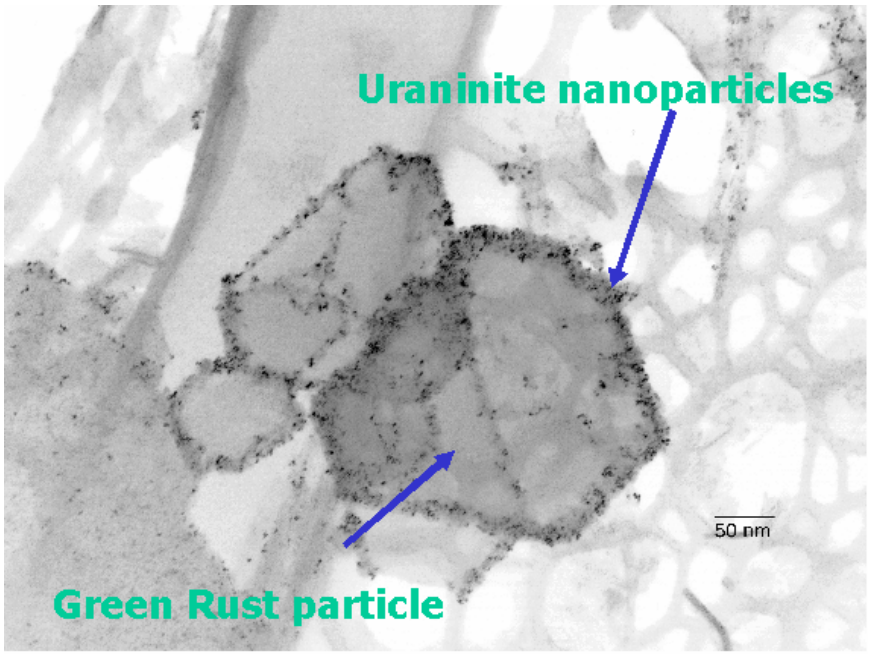

Figure 20. Uraninite nanoparticles on a green rust particle

The DOE has funded a project through its Environmental Management Science Program (EMSP) to examine the processes underlying the potential use of dissimilatory metal-reducing bacteria (DMRB) to create subsurface redox barriers for immobilizing uranium

and other redox-sensitive metal/radionuclide contaminants (Roden 2005). The results of these studies suggest that:

- the efficiency of dissolved U(VI) scavenging may be influenced by the kinetics of enzymatic U(VI) reduction in systems with relative short fluid residence times;
- association of U(VI) with diverse surface sites in natural soils and sediments has the potential to limit the rate and extent of microbial U(VI) reduction, and in turn modulate the effectiveness of in-situ U(VI) bioremediation; and
- abiotic, ferrous iron (Fe(II))-driven U(VI) reduction is likely to be less efficient in natural soils and sediments than would be inferred from studies with synthetic Fe(III) oxides.

A key implication of these findings is that production of Fe(II)-enriched sediments during one-time (or periodic) stimulation of DMRB activity is not likely to permit efficient, long-term abiotic conversion of U(VI) to U(IV) in biogenic redox barriers designed to prevent far-field subsurface U(VI) migration. Instead, ongoing DMRB activity will be required to achieve maximal U(VI) reduction efficiency.

The study of dissimilatory metal reducing bacteria (DMRB, the general class of which dissimilatory iron reducing bacteria are part) has recently led to some interesting nanoscience discoveries that may offer new directions for nanotechnology. While most biological oxidation-reduction reactions take place in the liquid phase using water soluble species, dissimilatory reductions require a process where the electron acceptor is a solid phase material. Understanding the details of this process has been the topic of much research, with the focus largely being on c-type (monomeric) cyctochromes (heme proteins generally bound in cell membranes) which are known to perform electron transport. In 2005, Derek Lovley, who discovered *Geobacter* in 1987, published research showing that conductive structures (known as pili or "microbial nanowires") only a few nanometers wide but microns long, are produced by *Geobacter*, are electrically conductive, and are indicated as being involved in electron transport (Reguera 2005). Subsequently, an international group (Gorby 2006) showed that other bacteria can be induced to produce nanowires (as small as 10 nm in diameter, but can reach hundreds of microns in length) when kept in an oxygen-starved state, are electrically conductive, and that this behavior is not limited to DMRB but might be a common bacterial strategy for efficient electron transfer and energy distribution. When in a community, the bacterial nanowires can cross and touch, and may allow for sharing of electrons among a network of bacteria. Figure 21 illustrates the bacterial nanowire reaching across organisms, and Figure 22 depicts a close-up image of a nanowire. The nanowires have been of great interest as a potential production and supply method of nanowires for other applications (such as sensors, nano-electronic components), as the basis of a possible remedial treatment approach, or as a component of microbial fuel cells.

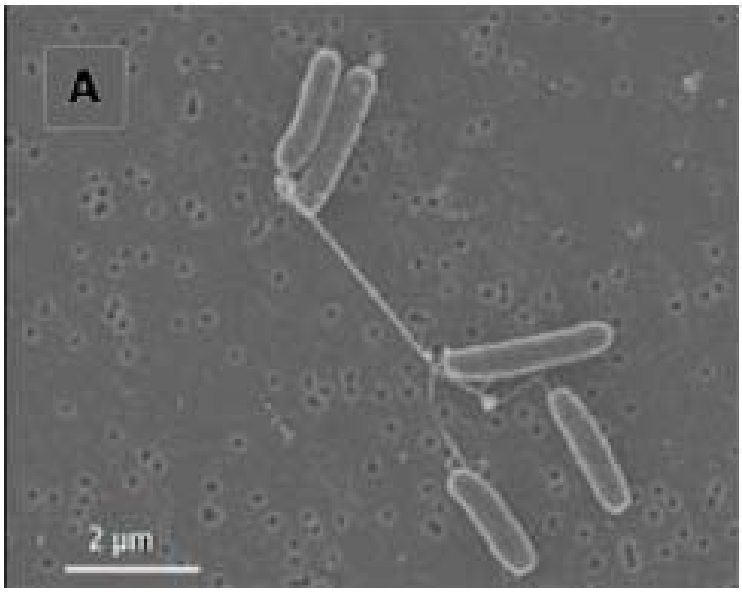

Figure 21. Scanning electron microscope image of *Shewanella ddeinensis* strain MR-1

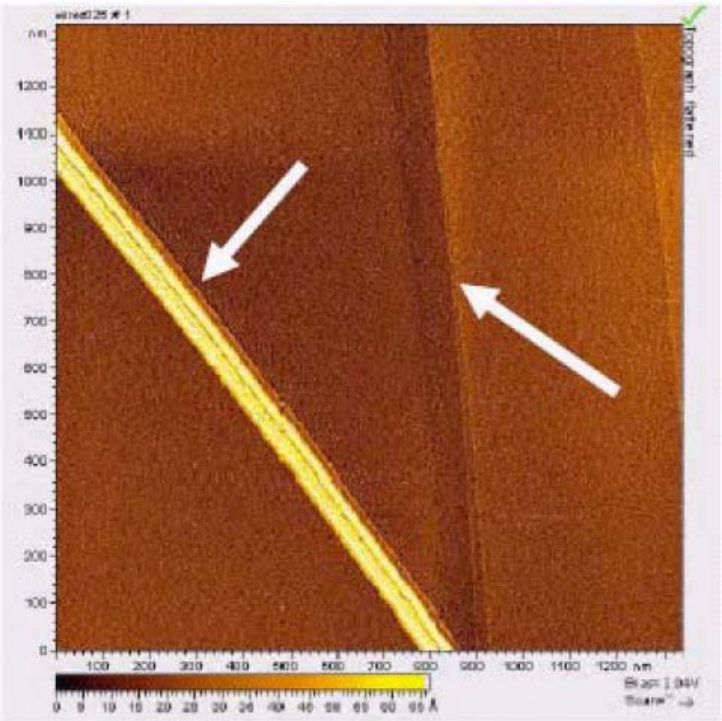

Figure 22. Scanning Tunneling Microscope (STM) images of isolated nanowires from wild-type MR-1, with lateral diameter of 100 nm and a topographic height of between 5 and 10 nm. Arrows indicate the location of a nanowire and a step on the graphite

In summary, the literature on microbially mediated reduction of U(VI) showed that U(VI) can be reduced to U(IV) by enzymatic activity of microorganisms, including:

- metal- and sulfate-reducing bacteria;
- U(VI) can be reduced either by pure cultures or by mixed indigenous cultures;
- U(IV) precipitates as uraninite (UO_2);
- complexation of U(VI) with organic and inorganic ligands can inhibit its reduction by microorganisms; and
- complexation of U(IV) may inhibit its precipitation.

Uranium reduction by bacteria is an example of bioremediation. As its advocates point out, bioremediation may be regarded as the oldest environmental technology of all, having existed virtually as long as the human species. Prior to 1989, bioremediation as a formal environmental technology was not widely known; it had a small number of advocates, though its claims were backed by considerable laboratory and academic work. The March 1989 Exxon Valdez disaster in Alaska and the subsequent use of bioremediation using naturally occurring marine organisms together with added nutrients, opened the way for bioremediation to become an established environmental remediation option. Economically, bioremediation usually offers great overall cost savings compared to competing technologies. In addition, risks tend to be smaller since contaminants are not transferred from one medium to another for processing, and there is no waste transportation involved. On the other hand, the bioremediation process may take much longer than chemical or physical treatment alternatives, requiring ongoing monitoring to ensure that progress is being made. When geological conditions are suitable and sufficient time is available, bacterial reduction of uranium is likely to be an attractive remedial alternative.

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2.8 Carbon Nanotubes (Fullerenes)

2.8.1 Background

After long being available only in research-level quantities, commercial-scale C-60 fullerene production at the "tons-per-year" level is now available. The price of larger fullerenes is still high and quantities available are still small. Commercial-scale production at affordable prices is the target of intense research; over 1,500 patents have been filed on various potential production technologies. No radionuclide remediation technology is currently available or apparently under consideration, though the concept has been discussed. Carbon nanotubes and fullerenes are of special interest since they have been subject of much research both as components in remediations systems (either as part of nano-composite membranes or as functionalized separation platforms), and as sensors (primarily through a field effect transition mechanism). They are also one of the icons of the nanotechnology age.

2.8.2 Description

Fullerenes (first discovered in 1985 by Robert Curl, Harold Kroto, and Richard Smalley), are a class of hollow, spherical, or ellipsoid molecules—composed entirely of carbon atoms—in a cage-like structure composed of pentagonal and hexagonal faces. They were named after the architect Richard Buckminster Fuller due to their similarity to his geodesic dome design, and are often referred to as "buckyballs". Fullerenes were the seventh allotropic form of carbon to be discovered (together with the two forms of diamond, the two forms of graphite, chaoit, and carbon (IV)). Their discovery led to Curl, Kroto, and Smalley receiving the Nobel Prize for Chemistry in 1996. Figure 23 provides a graphical representation of the 60-carbon atom containing C-60 fullerene, and Figure 24 illustrates a graphical representation of the 540-carbon atom containing C-540 fullerene.

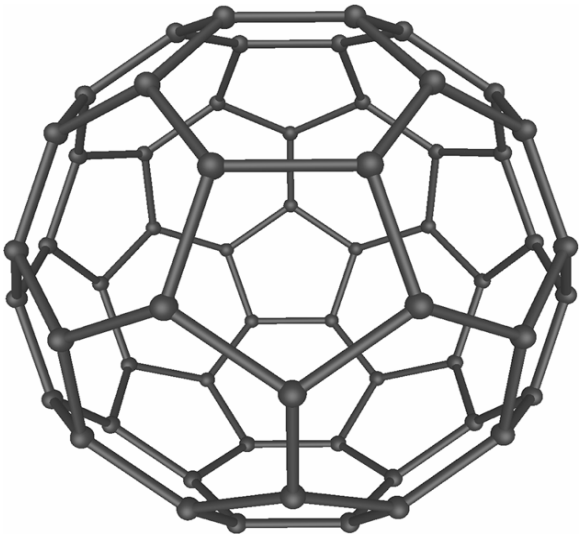

Figure 23. C-60 fullerene

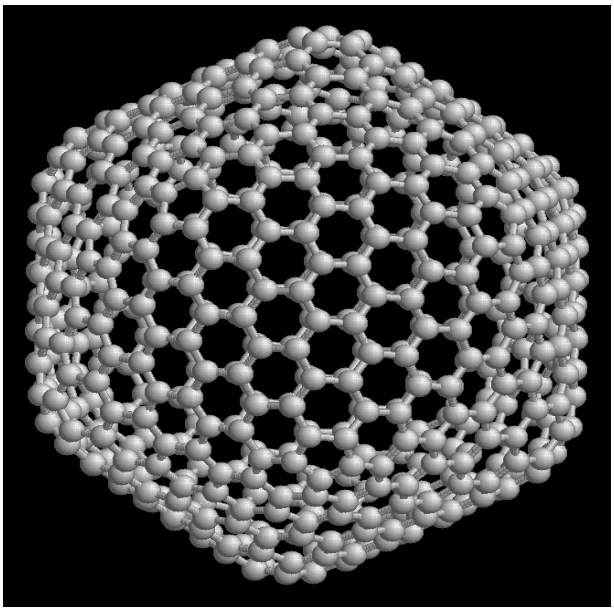

Figure 24. C-540 fullerene

An infinite number of spherical fullerenes are believed to be able to exist. Known forms include C-60, C-70, C-76, C-84, C-240, and C-540. All fullerenes consist of 12 pentagonal faces and a varying number of hexagonal faces. In general, for a fullerene C-n there will be 12 pentagonal faces and half of n minus 10 (n/2-10) hexagonal faces; thus, the C-60 fullerene has 12 pentagonal faces and 20 hexagonal faces.

Fullerenes have a rich and complex chemistry (Stevens 1994, Kadish and Roff 2000, Taylor 1995, Andreoni 2000, Hirsch et al. 2005) that led to the publication of over 15,000 academic papers within 15 years of their discovery. C-60 behaves like an electron deficient alkene, reacts readily with electron rich species, and participates in many reactions (including oxidations, reductions, nucleophilic additions, electrophilic additions, Diels-Alder reactions, and Friedel-Craft alkylations). This rich chemistry permits a wide range of fullerene functionalization and opens the way to designing functionalized fullerene for specific properties and purposes.

A large number of applications have been suggested for basic fullerenes and their functionalized derivatives. Potential applications include organic photovoltaics, polymer electronics, antioxidants, biopharmaceuticals, antibacterials, HIV inhibition, catalysts, water purification, MRI agents, optical devices, scanning tunneling microscopy, and atomic force microscopy (Nano-C 2006, Tang 2005, Da Ros et al. 2001).

Fullerenes have also been the subject of many studies related to radioactive materials. They are being extensively investigated as carrier species for medical radionuclides in cancer therapy (Saha et al. 2006, Dagani 2002, Braun 1999, Medical News Today 2005). It has been observed that in the combustion of coal, which contains small amounts of uranium, nanocrystals of the mineral uranitite are encased in fullerene-type cages. This

potentially provides an unanticipated pathway for radiation exposure (Utsunomiya et al. 2002). They have also been explored as a technology for radioactive waste management. DOE has determined that there are three major isotopes contributing to public radiation dose as a consequence of radionuclide releases—iodine-129, technetium-99, and neptunium-237—and fullerenes have been investigated as a sorbent for iodine (Schmett 2002). It is also worth noting that a structure closely related to fullerenes, the carbon nanohorn (Figure 25), has been suggested as a possibility for radioactive waste disposal.

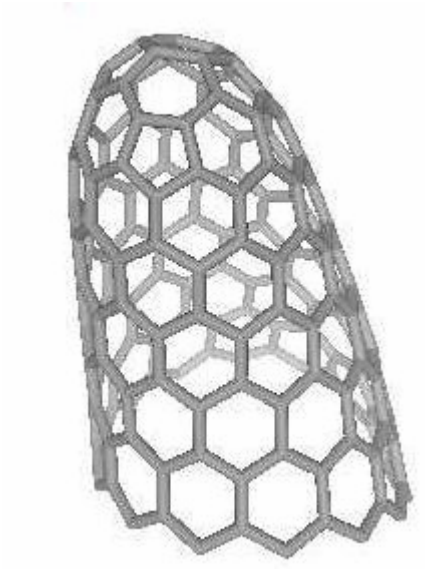

Figure 25. The carbon nanohorn

Though a vast amount of research has already been performed on basic carbon fullerenes, the real potential may lie in the fact that the work performed to date may only represent the tip of the iceberg. Many structures related to the basic fullerenes and the carbon nanohorn have been discovered. For example, the carbon nanocone (Figure 26) and "NanoBuds" (Figure 27) are relatively new materials developed by the Finnish company Canatu Oy (Canatu 2004, Nanowerk 2007) by combining carbon nanotubes and fullerenes. The resulting nanobuds possess properties of both materials (e.g., the electrical conductivity of carbon nanotubes with the chemical flexibility of fullerenes). Fullerene composites (Ltaief et al. 2006, Calleja et al. 1996, Barrera et al. 1994, Brabec et al. 1998, Eklund and Rao 2000, Prassides 2004) and hybrid materials, such as a fullerene-dendrimer-mesoporous silica hybrid (Nierengarten et al. 2004), have been described.

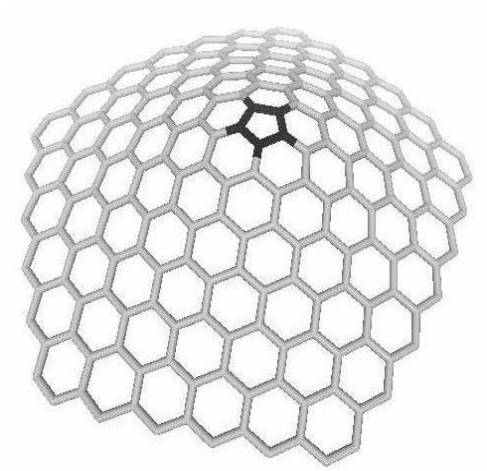

Figure 26. The carbon nanocone

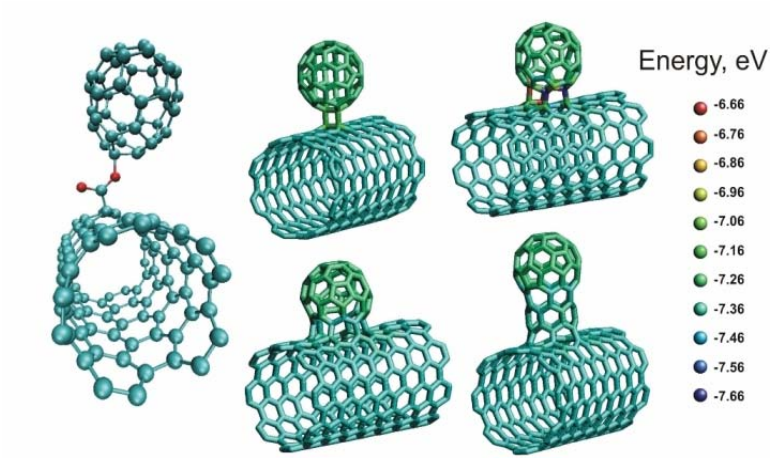

Figure 27. Carbon nanobuds

Further, there exists a potentially enormous class of "inorganic fullerenes". First described in 1992 (Materials Science Resource 2005), over 50 different types of inorganic fullerenes, and nanotubes have been reported in the technical and scientific literature, and include molybdenum sulfide, molybdenum selenide, tungsten sulfide, tungsten selenide, transition-metal chalcogenides, transition-metal oxides, transition-metal halides, in addition to mixed-phase, metal-doped, boron-based, silicon-based, and pure metal nanotubes (Sano et al. 2003, Lvayen et al. 2007, Fu et al. 2005, Parilla et al. 2004, Xia et al. 2004, Remskar et al. 2001, Parilla et al. 1999, Halford 2005), and "onion-like" fullerenes consisting of cages nested within other cages like Russian dolls (Cabio'h et al. 2005, Golberg et al. 1999).

2.8.3 Operational Considerations

As one of the longest known and most intensely investigated type of nanoparticle, fullerenes have been the subject of much study in terms of fate and transport. However, there is little consensus, other than the need for more research (Zepp and Westerhoff 2007, Wenger 2007, EIMS 2006, Handy and Owen 2006, Boxall 2007, Baalusha 2007, SETAC 2007, Drobne 2007). Recently, the results on investigations into the role of C-60 nanoparticles in relation to toxicity and bioaccumulation of xenobiotic organic compounds in *Daphnia magna* were presented (Johansen et al. 2007). The hypothesis was that C-60 nanoparticles may act as carriers of xenobiotic organic chemicals (nanovectors), but mixed results were observed and are detailed below.

- There was an increase in algal toxicity of atrazine with C-60 present; no changes in toxicity of methylparathion towards algae and daphnia.
- There was a decrease in the toxicity of pentachlorophenol (PCP) towards algae and daphnia after addition to C-60 suspensions.
- There was an increase in the toxicity of phenanthrene towards algae and daphnia in C-60 suspensions since the sorbed phenanthrene is bioavailable.
- The uptake and excretion rates of phenanthrene and PCP were not significantly affected by addition to C-60 suspensions.

Also, results on investigations into the effects of C-60 fullerene nanoparticles on soil bacteria and protozoa (Johansen et al. 2007) showed that fullerenes seem to have no, or only moderate, effects on the soil microbial community (regarding the number and viability of bacteria and protozoa). The genetic diversity of bacteria and protozoa seems to be altered slightly, but the mechanism behind the diversity changing effect is unclear (possible direct toxic effects on some of the microorganisms or indirect effects by sorption of nutrient or inhibiting factors in the soil). The conclusion was that since various fullerenes are very recalcitrant, and their production is expected to increase to very large quantities, it is important that their fate and ecotoxicology in complex environmental matrices be evaluated thoroughly in regards to transport, degradation, toxicology, and interactions with xenobiotics, and that there is a need for standardized methods for exposure of nanomaterials to organisms *in vitro* and in more complex systems.

2.8.4 Summary of Environmental Potential

Carbon nanotubes, and closely related materials, such as carbon nanohorns and carbon nanobuds, combine unique properties per se (such as greatly enhanced flow rates of water through the inside of the tubes over what would be expected from current theories) with the broad potential that results from a rich and complex chemistry. The range of applications is similarly wide, including both the development of advanced separatory processes (such as nanofiltration and reverse osmosis) and the development of nano-enabled sensors with the carbon nanotube acting as the sensing element. Carbon nanotubes have already been investigated for application to DOE's three major problem isotopes (iodine-129, technetium-99 and neptunium-237) contributing to public radiation

dose. Carbon nanotubes are one of the longest known and most widely investigated type of nanoparticle, with research including hybrid products formed with other nano-structured materials (such as dendrimers). Given the extremely broad range of possibilities and the level of research interest, the likelihood of environmental technologies resulting from carbon nanotubes is assessed as very high.

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3.0 Nano-Enabled Sensor Technologies

3.1 Introduction

3.1.1 Basics

Nanosensors are chemical sensors possessing a nanoscale sensing element. A chemical sensor is a device capable of providing quantitative or semi-quantitative information on a chemical species (or analyte) through calibration, and then brought into direct contact with the species in its environment. According to the definition given by the International Union of Pure and Applied Chemistry (IUPAC), a chemical sensor is:

> "A device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated. Chemical sensors contain two basic functional units: a receptor and a transducer part. Some sensors may include a separator which is, for example a membrane (IUPAC 1997)."

The receptor part of a sensor is defined by IUPAC as:

> "The chemical information is transformed in it into a form of energy, which maybe measured by the transducer. The receptor part maybe based upon various principles: physical, chemical or biochemical (IUPAC 1997)."

The transducer part of a sensor is defined by IUPAC as a:

> "Device capable of transforming energy carrying the chemical information about the sample into a useful analytical signal (IUPAC 1997)."

In addition, a sensor may include an output system, which processes the transducer output into a useable form and relays it to the outside world. In contrast to a sensor, a chemical analysis (or assay) method or system requires many more processing steps than simply bringing a device into contact with the analyte, and frequently involves the use of additional reagents. It is important that the receptor and transducer parts of a sensor are closely integrated. As an example of a receptor and transducer combination, imagine a very small, reed-like beam with a reflective surface, capable of vibration that can be measured by a laser. In its basic state, the beam will vibrate with one frequency. If part of the surface of the beam is covered with a ligand that will bind highly selectively with a target analyte, then in the absence of the analyte, it will vibrate with a second, different frequency; in the presence of the analyte, it will vibrate with a third, yet again different frequency that is a function of the analyte concentration. In this scheme the ligand is the receptor and the beam/laser system is the transducer; the sensor operates by optical

transduction of a chemical binding event. Receptor events may be transduced by electrical, electrochemical, piezoelectrical, optical, magnetic thermal, mass sensitive, or other means.

3.1.2 Chemical Sensors

Chemical sensors are used in many settings, including:

- Medical and health care arena for clinical diagnosis, drug screening, etc.;
- Pharmaceutical development, biotechnology, microbiology, bacteriology, virology, genomics, and proteomics research;
- A vast range of industrial process control;
- Industrial effluent and pollution control;
- Safety;
- Environmental monitoring; and
- Defense and security (chemical and biological weapons, explosives, and narcotics detection).

The United States chemical sensor market is valued at approximately $3 billion per year, of which between one half and two thirds is for medical diagnostics, and much of the remainder is for gas sensors. The market is growing; this is a result of past sensor development research and, in turn, is contributing to current and future research for even better sensors. The characteristics of an ideal chemical sensor include:

- Inexpensive—advantageous on its own merits and allows use of multiple detectors in arrays;
- Low operating costs;
- Robust;
- Reliable;
- Reversible;
- Continuously useable;
- High specificity;
- High selectivity;
- High sensitivity;
- High accuracy;
- Repeatability;
- Fast speed of response;
- Broad dynamic range;
- Insensitivity to (or ability to compensate for) interference by factors such as temperature, pH, ionic strength, electrical and magnetic fields, etc.;
- Small size for in-situ (biological or geological use); and
- Minimal perturbation of the sample.

Nanotechnology offers the promise of providing nanosensors capable of achieving many of these ideal characteristics, particularly those associated with speed, selectivity,

sensitivity, and size reduction. As a consequence, nanosensor development is one of the most active areas in the whole of nanotechnology. There are a number of major drivers for this activity. The first is miniaturization of sensors, which has been a pronounced trend in sensor development for the past 50 years. Some advantages of miniaturization are obvious. Smaller size:

- leads to less material used in fabrication, enabling mass production contributing to lower cost and broadening market availability.
- leads to reductions in weight and power consumption, which dramatically increase the versatility and range of options for use, and
- permits reduction of sample size and decrease in any reagent consumption.

3.1.3 The Trend towards Miniaturization

All of the preceding factors have encouraged the trend towards microsensors over the past decades, but the move to the nanoscale invites factors beyond the simple continuation of miniaturization.

- First, the new properties that are realized at the nanoscale and that have been partly discussed in earlier sections can be used in either the receptor or transducer parts of the sensor.
- A second nanoscale factor is that there are some inherent benefits in working directly at the molecular level where the sensing phenomena take place.

A study that directly asked the question of whether smaller is better for sensors (Kopelman and Dourado 1996) examined optical sensors and formalized the specific advantages of having nanoscale dimension sensors. In most instances, there is an explicit functional dependence of optode characteristics on the sensor radius (r), with the absolute detection limit decreasing with the cube of the radius (r^3), and the response time decreasing with the square of the radius (r^2). Other features that improve, as sensors get smaller, include sample volume, sensitivity, invasiveness, spatial resolution, dissipation of heat in sensor and/or sample, and materials cost. A third nanoscale factor is that fabrication advances in the semiconductor and related industries, together with the coming of control of fluids on the microscale, has allowed the integration of many laboratory processing steps into a single device, and given rise to the concept and implementation of the LOC discussed in Section 3.2.

The development of the LOC is directly related to a second major driver of nanosensor development—the analytical needs of the biotechnological and biomedical industries. Across many areas of biologically-related research, including the enormous areas of pharmaceutical and proteomic research, there is a need for cellular-level and massive-throughput analytical and sensing capabilities. The large-scale, low-cost manufacturing potential for nanosensors, and the greatly reduced reagent demands associated with sample preparation in their use, make them extremely attractive tools. In the medical field, early detection and diagnosis can greatly reduce the cost of patient care associated

with advanced stages of many diseases. Similarly, point-of-care sample analysis and real-time diagnosis can provide major savings for treatment of less serious conditions.

An additional issue, not so much a driver for sensor development, but rather an enabling aspect in comparison with the development of remedial technologies, is the comparative ease of sensor development. Past experience, particularly in federal agencies with environmental responsibilities (such as EPA, DOE, and Department of Defense (DoD)), indicates that, generally, the time to maturity for a sensor development project (i.e., the duration of the entire effort from initial idea, through proof-of-concept, scientific development, engineering development, prototyping, demonstration, and deployment) is considerably shorter and less complex than the time to maturity for a remedial technology development project. Further, in terms of market penetration, or the transition from first being commercially available to being widely deployed, the timeline is shorter and the regulatory hurdles are much lower. Since the risks associated with sensors are much smaller than with remedial technologies and the development costs are smaller, even when allowance is made for the shorter development time, environmental sensors are a much more attractive investment than remedial technologies. This situation is likely to apply to nanotechnologies, as well as to conventional technologies.

3.1.4 Opportunities

In the environmental area (in general) and the remediation of radionuclides (in particular), there is a marked need for sensors with:

- lower fixed and operating costs;
- better performance in terms of sensitivity and specificity; and
- more versatility in terms of portability and field operability.

Control of remedial processes, contaminant detection, compliance monitoring, and environmental decision-making should all benefit from sensors with molecular level detection and improved overall performance. Current methods are costly, time-intensive, and limited (Sandia 2005). The use of in-situ or field operable sensors eliminates risks and costs associated with sample collection, handling, custody, transport, and storage. DOE's Savannah River Site requires manual collection of nearly 40,000 groundwater samples per year, with a cost of between $100 and $1,000 per sample for off-site analysis (Looney and Falta 2000).

It is anticipated that nanotechnology will have a bigger impact in providing sensors for radionuclide remediation than it will in providing remedial technologies, due to:

- the well-structured basic understanding of sensor technology development;
- the shorter, less expensive timelines for sensor development; and
- the existing level of activity surrounding nanoscale sensor development.

The number of development efforts for radionuclide sensors is still very small, but this is because most efforts are being put into the medical and biotechnology areas, where there is a much larger potential market. Given our level of understanding of how receptors are integral to sensors and our level of understanding of how to design receptors for radionuclide species, it is a small extrapolation from the current, biologically oriented state-of-the-science to a future state-of-the-science, where radionuclide sensors can be easily realized. The following sections describe sensor technologies, or technology concepts, that can be comfortably extrapolated to radionuclides. As with Section 2 on remedial technologies, since extrapolation is involved, the survey cannot be comprehensive but rather seeks to provide information on reasonable possibilities that may yield sensor technologies in the near future.

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3.2 "Lab-on-a-Chip"

A Lab-on-a-Chip (LOC) device, also known as a micro-total-analytical system (microTAS) or microfluidics device, is a device that can integrate miniaturized laboratory functions (such as separation and analysis of components of a mixture) on a single microprocessor chip using extremely small fluid volumes on the order of nanoliters to picoliters. From a technology categorization perspective, LOCs can be viewed as a subset of microelectromechanical systems (MEMS) and combine miniaturized or novel sensing systems, fluid flow control concepts from microfluidics, and the suite of fabrication techniques (such as material deposition, material removal, surface patterning, and electrical property modification) used by the semiconductor industry.

Currently, the main commercial applications of LOCs are in the medical and biotechnological fields, where it is anticipated that developments so far are the heralds of a technological revolution. In the same way that miniaturization changed computers from machines of limited capabilities occupying large rooms to small and easily portable yet powerful technology of today, over a period of a few decades, medical, biotechnological, and chemical analysis is expected to move from room-sized laboratories to microchip-based devices housed in hand-held or small portable readout consoles. Figure 28 shows an example of an LOC device that was tested on the International Space Station in 2007.

Figure 28: LOC device tested on the International Space Station in 2007

At the heart of LOC devices are "chips", ranging in size from a fingernail to a credit card, fabricated using processes adapted from the printed circuit industry such as lithography, chemical etching, and laser machining. Figure 29 illustrates an impression of the size of the chip. Figure 30 provides a functional diagram of LOCs.

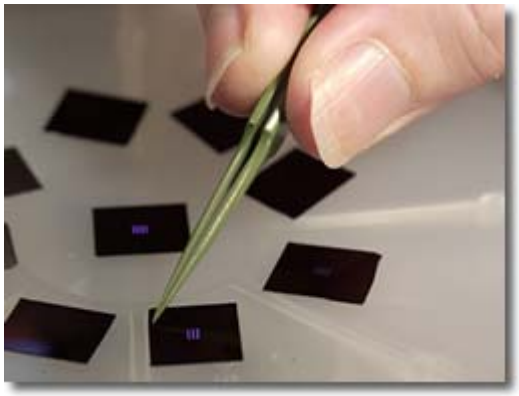

Figure 29. A comparison of the size of LOCs

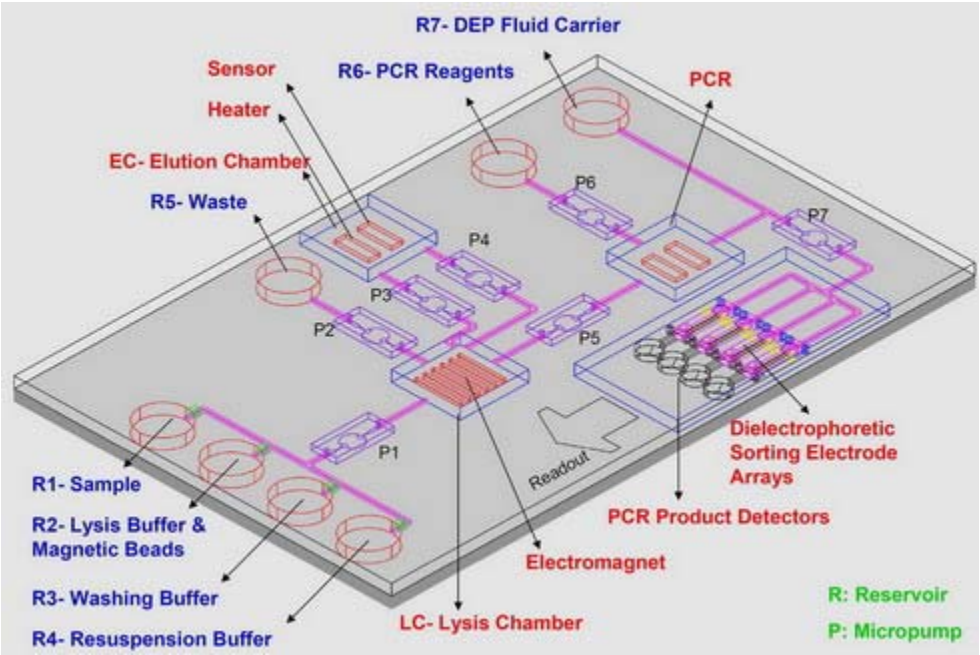

Figure 30. Functional diagram of LOCs

In a manner similar to the production of printed circuit boards using techniques such as embossing and molding, microstructures (such as channels for liquid flow and pits for mixing and reactions) are made on the chip by depositing layers of material on top of one another on a surface, then patterning and selectively removing material to form a feature. A flat top surface or lid is attached to enclose the channels or mixing pits, and reagents can be driven around the system by pneumatic, electromotive, or capillary systems.

The LOC was first conceived by Michael Widner at Ciba-Geigy (now Novartis) in the 1980s, described conceptually in 1990 (Manz et al. 1990) with a groundbreaking work being published in 1992 (Harrison et al. 1992). Further development occurred as a new area of discovery—microfluidics—was developed in the 1990s. Microfluidics is an

interdisciplinary field dealing with the behavior and control of extremely small volumes of fluids and the design of systems that use these small volumes. Though most commonly encountered in ink-jet printers, the vast majority of microfluidics applications have been in biotechnology research, and some experts even regard it as a branch of biotechnology. In some ways, Microfluidics parallels nanotechnology in that the behavior of fluids at the microscale can differ substantially from the behavior at the macroscale; phenomena such as surface tension, heat conduction, and fluidic resistance start to become important, and issues such as evaporation, absence of turbulent flow, and the threat posed by presence of air bubbles are critical to system design.

Initially, much of the impetus for continued development of LOCs came from the Human Genome Project, a 13-year project coordinated by DOE and the National Institutes of Health (NIH) that began in 1990 and was completed in 2003. Currently, much of the impetus for the continued development of LOCs comes from the desire for point-of-care medical diagnostics, whether in the doctor's office, on a spacecraft, or other remote location. Additionally, development research is driven by the continued need for miniaturization, both to reduce the costs and the environmental impacts of research (green analytical chemistry). The LOC concept, already significant, is still considered to be in its infancy. Development research continues in many areas. In the area of fabrication materials, LOCs constructed using soft lithography techniques, rather than silicon microchip fabrication processes, are being investigated. Soft lithography is an alternative to silicon-based micromachining that uses replica molding of nontraditional elastomeric materials to fabricate stamps and microfluidic channels. In an extension to the soft lithography approach, multilayer soft lithography, with which devices consisting of multiple layers may be fabricated from soft materials, is being used to build active microfluidic systems containing on/off valves, switching valves, and pumps entirely out of elastomer. The softness of these materials allows the device areas to be reduced by more than two orders of magnitude compared with silicon-based devices. The other advantages of soft lithography (such as rapid prototyping, ease of fabrication, and biocompatibility) are retained (Unger et al. 2000).

Environmental LOCs are also being investigated. An environmental LOC project is being funded by EPA with objectives to create a novel, nanomaterial-based submersible microfluidic device, exploiting unique properties of metal nanoparticles and carbon nanotubes for rapidly, continuously, and economically monitoring different classes of priority pollutants. The project also seeks to understand the relationship between the physical and chemical properties of these nanomaterials and their observed behavior. The challenge addressed is to help transform the LOC concept to an effective environmental monitoring system, and involves the examination of nanoparticle and nanotube materials for the separation and detection processes, respectively (Wang 2007). In addition, the NIH is supporting the development of a point detection disposable LOC with built-in mercury precursor electrodes for heavy metal detection (Ahn 2006).

Within these development efforts, it is also recognized that for novel and innovative technologies, even those that have an established market presence, close communication between developers and future users is essential. For example, in the United Kingdom,

research collaboration between five leading universities in the healthcare technology assessment arena and a group of industrial partners—Multidisciplinary Assessment of Technology Centre for Healthcare (MATCH) —is conducting a survey of LOC point-of-care device manufacturers. Point-of-care in this context is defined as "analytical testing performed outside the central pathology laboratory using a device or devices that can be easily transported to the vicinity of the patient" (MATCH 2006). The aim is to assess the value of LOC for the diagnosis of cardiac-related problems using case studies, and to develop methods to shorten the time and decrease the costs of LOC development.

3.2.1 Summary of Environmental Potential

The LOC has great potential for addressing environmental needs. The technology platform is mature and well-established, and as other nano-enabled sensing technologies are developed, integration into the LOC should be facile. The twin features of rapid sample throughput and field portability should make the LOC a valuable tool in filed operations, particularly in circumstances such as the EPA Triad approach, where real-time monitoring is required to guide the progress of remedial work.

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3.3 Microcantilever Sensors

Microcantilever sensors are a technology which may develop into sensing systems for radionuclides, or is at least an example showing the potential and emergence of a new generation of highly sophisticated but flexible sensors. From a mechanical engineering perspective, a cantilever is simply a beam supported at one end and capable of defined bending and vibrational behavior. A microcantilever is simply a very small cantilever, the properties of which can be understood from basic engineering principles.

The microcantilever was first developed in 1986 (Binnig et al. 1986) for use in Atomic Force Microscopy (AFM), the premier tool for nanoscale imaging and measuring. In AFM, an extremely sharp microscale tip, (with a tip radius of a few nanometers) connected to the end of a microcantilever (up to 10 nm thick, about 500 nm wide and about 2,500 nm long, and fabricated from Si or Si_3N_4), is positioned extremely close to the surface of a sample and the sample, is then moved beneath the tip. Interactions between the surface of the sample and the end of the tip arising from atomic forces (such as Van der Waals force, electrostatic force, magnetic force, or capillary force) attract or repel the tip (depending on mode of operation) and bend the microcantilever. Reflecting a laser beam off the cantilever and monitoring the beam's deflection with photodiode arrays measures the amount of bending. A graphical representation of the AFM sensing components is provided in Figure 31, and a Scanning Electron Micrograph of a microcantilever biosensor used for DNA detection is shown in Figure 32.

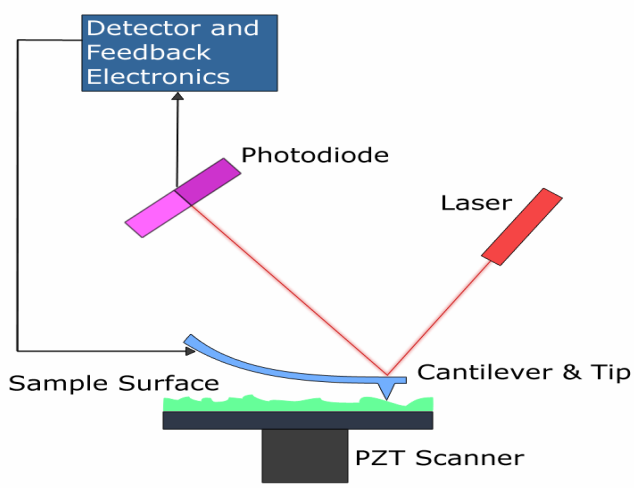

Figure 31. Principle of operation of the atomic force microscope

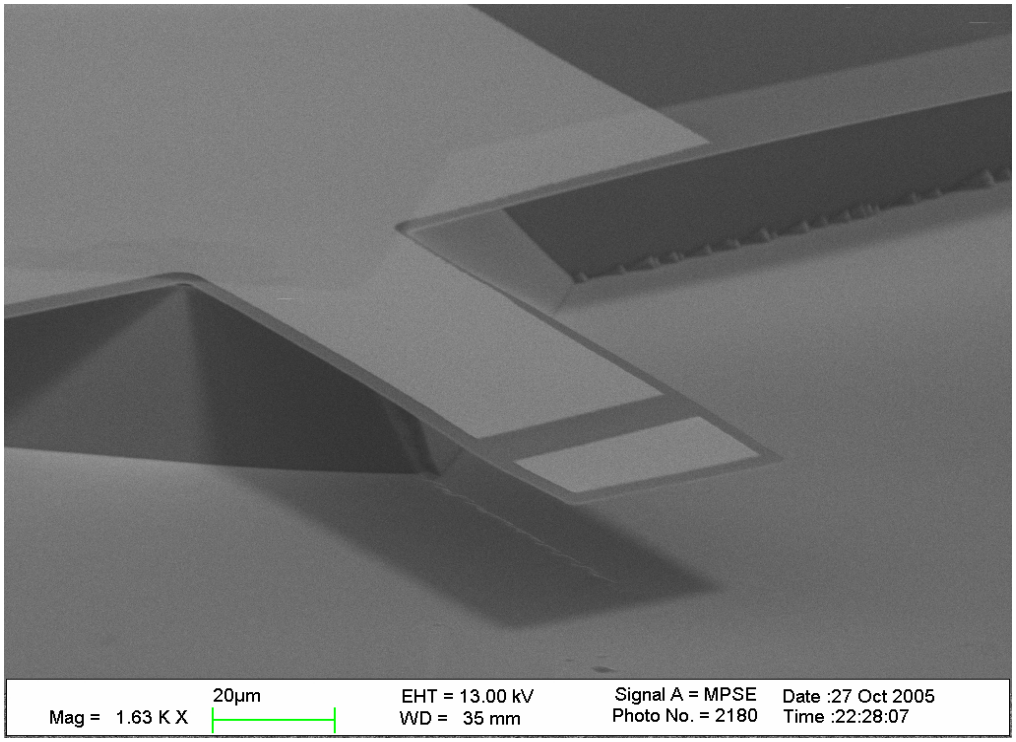

Figure 32. Scanning electron micrograph of fabricated microcantilever biosensor used for DNA detection

The microcantilever is the simplest MEMS device. Early work soon demonstrated the versatility of the device in AFMs, with the microcantilever able to perform in air, liquid, or vacuum and across a range of temperatures. It also demonstrated the extreme sensitivity of the AFM to environmental effects and impurities, and the need to control these in making accurate measurements. However, studies on overcoming these issues also showed that the sensitivity of AFM to these environmental factors could be turned around, allowing the AFM to be a sensor for these same factors. For example, a microcantilever fabricated from silicon and coated with an aluminum surface for reflection of the laser beam can act as a "bimetallic strip" and respond to temperature changes. If a thermal event takes place on the cantilever surface, the silicon and aluminum expand to different extents and the cantilever bends, allowing the cantilever to act as a calorimeter of near-ultimate sensitivity. Similarly, if the microcantilever is given an absorbent coating that can attract water and is allowed to vibrate in dry air, it will have a natural frequency of vibration; changes in humidity change the mass of the microcantilever, and thus change the frequency of vibration, allowing it to act as a humidity sensor. From this, it is a short step to the concept of coating the microcantilever with a chemical functionality that binds selectively with a target analyte. In the absence of the analyte, the microcantilever vibrates with one frequency, while in the presence of the analyte, binding with the microcantilever coating occurs and vibration takes place at a frequency directly related to the degree of analyte binding—hence concentration.

A related sensing mode is that the surface of the microcantilever can be coated with a layer of material that contains the chemical functionality able to bind selectively with a

target analyte. If this layer expands or contracts as the analyte is bound, then bending of the microcantilever occurs in a manner analogous to that of the bimetallic strip used for thermal sensing. The degree of bending is directly related to analyte concentration. This behavior was the basis of a microcantilever radionuclide sensor development project at ORNL. As described in Section 2.3 on SAMMS, if a head group at the end of a long organic chain molecule can interact strongly with a substrate, then a closely packed molecular monolayer of the chain molecules aligned with the chains pointing outwards from the substrate surface can form spontaneously when the two are brought into contact. The tail end of the organic chain can be functionalized prior to, or after, self-assembly using chemical functionalities selective for a targeted species. Thiol (S-H) head groups and a gold substrate form an excellent pairing for this type of behavior, and the self assembly of alkanethiols has been observed to produce surface stress in the gold substrate (Berger et al. 1997).

Silicon and closely-related materials have been the main materials of construction for microcantilevers. Silicon has been recognized as an outstanding mechanical material for over a quarter of a century (Petersen 1982). However, silicon is not the only fabrication material under investigation. Chemical sensing with micromolded plastic cantilevers and production issues have been explored (McFarland and Colton 2005).

In addition to microcantilevers based on silicon, plastics; and related materials, nanostructures (such as single-walled carbon nanotubes (SWCNT)) have been explored for gas-sensing applications (Hsu 2007). The approach uses the fact that SWCNTs are capable of interacting with the gaseous species—either directly through surface adsorbtion, or indirectly by using a polymer analyte coated on its surface—and the higher surface-to-bulk ratio available with a nanostructure leads to higher sensitivity and shorter response time. As with other microcantilevers, the effect of bound or adsorbed species is manifested either as a change in resonant frequency (which can be detected by using a Wheatstone bridge circuit), or as an increased surface stress (which can be detected by measuring the change in the capacitance value through comparison with a specific reference capacitor). Hsu's work involved successful simulation, fabrication, and manipulation of the SWCNT; development and simulation of a capacitive sensing circuit layout; and consideration of packaging and integration issues, including use of a "nanoglue" developed at Rensselaer Polytechnic Institute, based on the processing of a self-assembled molecular monolayer and capability of bonding completely dissimilar materials.

Among the drivers for further development was the widespread need for portable, real-time, in-situ chemical, physical, and radiological sensors in a variety of applications including the characterization and monitoring of mixed waste, ground water, contaminated soil, and process streams. Microcantilever-based sensors were recognized as a potential solution for this need. They also provide excellent sensitivity for important metal ions in solution such as Hg^{2+}, CrO_4^{2-}, Sr^{2+}, and TcO^{4-}. The ability of the microcantilever to detect cesium (Thundat et al. 1999, Ji et al. 2000a) (though irreversibility problems were observed) and chromate (Ji et al. 2000b) was demonstrated;

concentrations below the parts per billion level were obtained with exceptional selectivity even in the presence of other interferences.

Fundamental microcantilever research at ORNL showed that adsorption-induced changes in the spring constant of a cantilever, leading to errors in the calculation of adsorbed mass from shifts in resonance frequency (Thundat 2002). Simultaneous measurement of resonance frequency and adsorption-induced bending was shown to allow the change in spring constant to be determined. A silicon microcantilever with gold coating on one side was found to respond selectively and sensitively to Hg(II) ions in solution, and while modification of the Si surface with a silane reagent did not change the response to Hg, modification of the gold surface with octanethiol greatly retarded the rate of deflection, indicating the Hg(II) is reacting with the gold surface. The surface charge on the gold-solution interface is postulated to reduce Hg(II) to a surface amalgam. Modification of the gold surface with a monolayer 1,6-hexanedithiol makes the surface sensitive and selective for $(CH_3)Hg^+$ adsorption-induced deflection. Na^+, K^+, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, and Ni^{2+} in solution do not interfere with the response of the microcantilever to Hg. Gold coated cantilevers with chemically modified surfaces respond sensitively to Ca^{2+} ions at a concentration of 10^{-9} M. The sorption of a monolayer of 2-(4-mercaptophenoxy)-N, N-diethyl-acetamide, as well as the agent bis (11-mercaptoundecyl) phosphate were shown to detect Ca^{2+} ions, although the former was more selective. A self-assembled monolayer of L-cysteine on a cantilever coated with gold on one side was shown to be effective for the detection of a concentration of 10^{-10} M Cu^{2+}. Both the Ca^{2+} and the Cu^{2+} were relatively free from interference by each other and Na^+, K^+, Pb^{2+}, Zn^{2+}, Cd^{2+}, and Ni_2 in solution (Thundat 2002).

Subsequent work showed that electrochemically-active metal ions (Cu, Cr, Hg and Pb) could be detected by the novel approach of using a cantilever as a working electrode since electrodeposition of electro-active metal ions on cantilever surface results in cantilever bending. Together with the observation that that the cantilever bending is extremely sensitive to electrochemical current in the solution, this has led to the development of a technique where the cantilever serves as a reference/counter electrode for electrochemical reactions occurring on another working electrode (Thundat et al. 2006), with work continuing towards the development of field-deployable, miniature sensors with extremely high sensitivity, exceptional selectivity, and the ability to be integrated into a wireless communication system that will allow real-time data to be provided on concentration and speciation of multiple contaminants and their variation with time.

Work has also continued on microcantilevers functionalized with metal-binding moieties. Gold-coated sides of silicon nitride microcantilevers functionalized with the metal-binding protein AgNt84-6 have been demonstrated to be sensors for the detection of heavy metal ions, such as Hg^{2+} and Zn^{2+} (Cherian et al. 2003). On exposure to $HgCl_2$ and $ZnCl_2$ solutions, the microcantilevers underwent bending corresponding to an expanding gold side, while exposure to $MnCl_2$ solution did not result in a similar bending, indicating a weak or lacking interaction of Mn^{2+} ions with the AgNt84-6 protein. The microcantilever bending data were consistent with data from electrophoresis that showed

protein interaction with Zn^{2+} ions but not with Mn^{2+} ions, demonstrating that microcantilever bending can be used to discriminate between metal ions that bind and do not bind to AgNt84-6 protein in real time.

3.3.1 Summary of Environmental Potential

Microcantilever sensors are one of the few nano-sensor technologies that have already been investigated with the detection of radioactive species in mind. The technology is very flexible; all that is needed for detection of a species is a coating with a chemical functionality capable of binding the target species. The technology is well-established, reliable, and sensitive—its origin in the AFM makes it a gateway technology for the nanotechnology age—and is easily integrated into the LOC platform. The versatility of the technique is further expanded by the fact that many materials, including innovative nanomaterials such as carbon nanotubes, may be usable as the cantilever.

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3.4 Spectroscopic Sensors

Spectroscopy is the scientific study of the absorption, emission, or scattering of electromagnetic radiation by atoms, molecules, ions, solids, liquids, or gases. The underlying and unifying phenomenon behind all types of spectroscopy is that the interaction of electromagnetic radiation with any type of matter can cause transitions between quantized energy levels (often, though not always, electronic energy levels) of the atoms or molecules. Since so many of these transitions can occur and can be influenced and modified by other phenomena, spectroscopy provides the potential for enhanced chemical analysis and sensing. The list of spectroscopic techniques and sub-techniques is large and continually increasing. A partial sampling of these techniques includes:

- Absorption spectroscopy
- Atomic absorption spectroscopy
- Atomic emission spectroscopy
- Atomic fluorescence spectroscopy
- Attenuated total reflectance spectroscopy
- Auger electron spectroscopy
- Cavity-ringdown laser absorption spectroscopy
- Electron paramagnetic spectroscopy
- Electron spectroscopy
- Electron spin resonance spectroscopy
- Extended x-ray absorption fine structure spectroscopy
- Fluorescence spectroscopy
- Fluorescence correlation spectroscopy
- Gamma-ray spectroscopy
- Image correlation spectroscopy
- Infrared spectroscopy
- Intracavity-absorption spectroscopy
- Laser spectroscopy
- Laser-induced fluorescence
- Mass spectrometry
- Mossbauer spectroscopy
- Nuclear magnetic resonance spectroscopy
- Multiplex or frequency-modulated spectroscopy
- Raman spectroscopy
- Resonance-ionization spectroscopy
- Tunable diode laser absorption spectroscopy
- Surface-enhanced raman spectroscopy
- UV-vis absorption spectroscopy
- X-Ray spectroscopy

Phenomena based on nanoscale effects are being examined in and by many of these types of spectroscopy. Some examples include:

- Nanosensors for nitric oxide using cytochromes have been examined and show a fast, reversible, and linear response up to 1 mM nitric oxide with a detection limit of 20 μM (Barker et al. 1998).
- A fluorescence nanosensor for Cu^{2+} ions using surface functionalization of silica particles with trialkoxysilane derivatized ligand and fluorescent dye has been investigated (Brasola et al. 2003).
- PEBBLE nanosensors, in the 20 to 200 nm size range, have been made for zinc detection using two fluorescent dyes (one sensitive to zinc and the other as a reference) localized in a polymer matrix by a microemulsion (Sumner et al. 2002).
- A simple colorimetric technique for the detection of small concentrations of lead, cadmium, and mercury) using reversible chelation/aggregation process for functionalized gold nanoparticles has been developed (Kim et al. 2001).
- A distributed Bragg reflector (a high-quality reflector used in waveguides and formed from multiple alternating layers of materials with varying refractive index) optical sensing element for organic solvents has been developed using stacks of Teflon®-like and gold nanoparticles. Absorption of organic vapors causes swelling of the composite and affects the reflectivity (Convertino et al. 2004).
- The first nanometer-scale anion sensing fluorescent spherical nanosensors have been developed (Brasuel et al. 2003).
- A rapid and sensitive fluorescence immunoassay has been developed for the simultaneous detection and identification of multiple harmful microorganisms using dye-doped silica nanoparticle-antibody conjugates (Zhao et al. 2004).
- The fabrication of submicron optical-fiber fluorescent sensors and particle-based fluorescent nanosensors has been reviewed, and the functional characteristics of miniaturized fluorescent sensors and their applications for quantitative measurement of intracellular analytes have been discussed (Lu and Resenzweig 2004).
- A nanoscale fluoroimmunoassay for the herbicide atrazine in an LOC has been developed using lanthanide oxide nanoparticle labels (Koivunen et al. 2004).

As these examinations indicate, most spectroscopic sensing methods detect the binding of a target species to a receptor by incorporating a fluorescent moiety into the receptor and then examining the fluorescence behavior. Fluorescence spectroscopy analyzes the fluorescence of a material, where fluorescence is a non-thermally originating luminescence phenomenon in which a molecule or other species absorbs a photon at one wavelength (usually in the visible range), and then re-emits another photon with a longer wavelength (usually in the ultraviolet range), with the difference in energy between the two photons becoming thermal energy through vibrational relaxation. Fluorescence can now reach down to the single molecule detection level and is such a powerful technique that, over the past decade, it has become the dominant tool in biotechnology and medical imaging (Geddes 2005). The following two examples demonstrate nanotechnologies that

incorporate the fluorescence spectroscopy tool, PEBBLE and Surface Plasmon Resonance.

3.4.1 Probe Encapsulated by Biologically Localized Embedding

A nanotechnology that incorporates the fluorescence tool is PEBBLE. PEBBLE nanosensors are sub-micron sized optical sensors designed specifically for minimally invasive analyte monitoring in viable, single cells. PEBBLE is a general term that describes a family of matrices and nano-fabrication techniques used to miniaturize many existing optode technologies. The main classes of PEBBLE nanosensors are based on matrices of polyacrylamide hydrogel, sol gel silica, and cross-linked decyl methacrylate. These matrices have been used to fabricate sensors for H^+, Ca^{2+}, K^+, Na^+, Mg^{2+}, Zn^{2+}, Cl^-, NO_2^-, O_2, NO, and glucose that range from 30 to 600 nm in size. A host of delivery techniques have been used to successfully deliver PEBBLE nanosensors into mouse cells (Monson et al. 2003, Park et al. 2003, Xu et al. 2001, Buck et al. 2004, Xu et al. 2002, Clark et al. 1999, Sumner et al. 2002). The PEBBLE nanosensor format offers the twin benefits of protecting fluorescent indicator dyes from interferents and allowing combination of multiple dyes, ionophores, and other components to create complex sensing schemes. It is the multifunctionality that is the main advantage of PEBBLE nanosensors for biological research. A conceptual representation is shown in Figure 33.

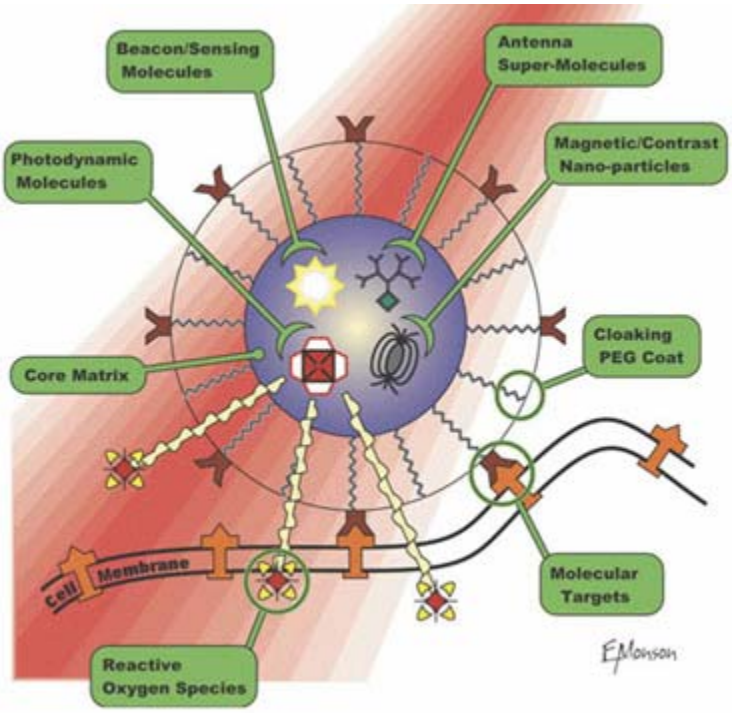

Figure 33. Conceptual representation of the multifunctionality of PEBBLE nanosensors

PEBBLE nanosensors were specifically developed for biological work since they have the advantages of a small size that permits intra-cellular biological measurements to be

made without causing cell mortality; a polymeric matrix able to contain a combination of indicator dyes, reference dyes, and catalysts (including some that might normally be toxic to the cell); fast response time; and the option of being calibrated by either ex-vivo or ex-vitro means. The use of both indicator dyes and reference dyes enables ratiometric fluorescent detection, which can correct for variations in excitation source intensity and minimizes the effects of photobleaching on quantitative measurements.

3.4.2 Surface Plasmon Resonance

While PEBBLE nanosensors offer a platform on which existing spectroscopic techniques can be mounted, a spectroscopy that offers great potential for chemical sensing and has achieved a much deeper understanding as a result of nanotechnology (specifically through the development of the new field of nanoparticle optics) is surface plasmon resonance (SPR) spectroscopy.

Comprehension of SPR first requires an understanding of the plasmon phenomenon. In physics, photons are regarded as the particle equivalent of quantized electromagnetic waves. From solid-state physics, it is also commonly understood that the electrons in a metallic crystal can be successfully modeled as a quasi-ideal gas, or plasma.. Oscillations in the charge density of this quasi-ideal gas can occur, and when waves are quantized as standing waves then the particle equivalent is known as a plasmon. Surface plasmons are plasmons confined to the surface of a material or the interface of plasma-containing material with some other material. They propagate parallel to the material surface and are evanescent waves that decay exponentially with distance from that surface; they are thus very sensitive to any changes at the surface. Plasmons can be excited by coupling with incident light to give the phenomenon of surface plasmon resonance.

Gold and silver are the classic metals for supporting surface plasmons, but metals such as copper, chromium, and titanium also support the phenomenon. When surface plasmon resonance is achieved on macroscale or mesoscale surfaces using very thin metal films, the plasmon wave can propagate across the surface for a distance of tens or hundreds of thousands of nanometers, but decays quickly as it moves outward from the surface. This is known as propagating surface plasmon resonance. Surface plasmon resonance can also be achieved on the nanoscale using metal nanoparticles, even though they are smaller than the wavelength of the light involved. In this case the plasmon wave oscillates locally around the nanoparticle. This manifestation of the phenomenon is called localized surface plasmon resonance (LSPR). A comprehensive review of LSPR spectroscopy and sensing is available (Willets and Van Duyne 2007).

The primary consequences of LSPR resonance include (1) localized electromagnetic field enhancement that is responsible for the intense signals observed in surface-enhanced spectroscopies, and (2) selective photon absorption and scattering (collectively called extinction), which can be easily monitored using UV-vis spectroscopy (Haes and Van Duyne 2002). Regarding the extinction behavior, theoretical considerations of the optical properties of nanoparticles (Haes et al. 2004) indicates that there are at least four different nanoparticle-based sensing mechanisms for transducing chemical-binding events into

optical signals: (1) resonant Rayleigh scattering from nanoparticle labels (analogous to fluorescent dye labels); (2) nanoparticle aggregation behavior; (3) charge-transfer interactions at nanoparticle surfaces; and (4) local refractive index changes. The plasmon resonance phenomenon thus provides a variety of approaches for measuring its behavior that can be exploited in the development of sensors.

Changes to the surface have major effects on this resonance. It has been observed that solutions of certain nanoparticles (e.g., gold) can give rise to intense colors; as far back as the medieval period, artists working in stained glass used this effect (see Figure 34). The origin of this effect, which is not manifested in the bulk material, is the absorption of energy in the ultra-violet region of the spectrum as a result of surface plasmon resonance. Changes to the surface of the gold particles (e.g., the binding of DNA or other bio material) have noticeable and easily measurable effects on the frequency of the surface plasmon resonance, and can be used as a sensing mechanism.

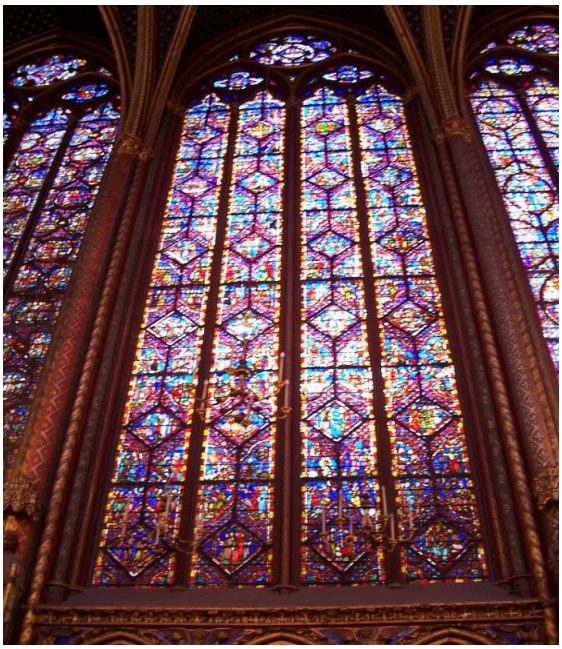

Figure 34. The colors in medieval stained glass are the result of surface plasmon resonance

The most acclaimed use of LSPR spectroscopy using nanoparticles has been the detection of a biomarker for Alzheimer's disease from synthetic and clinical samples (Haes and Van Duyne 2004, Haes et al. 2005). It has also been shown to detect small molecules, such as camphor (Zhao et al. 2006b). Further, with the appropriate recognition moiety, LSPR should be easily modifiable to detect metals and radionuclides. In fact, the feasibility of developing an SPR spectroscopy-based sensor, a technique very closely related, for a radioactive material (pertechnetate) has already been demonstrated (Anderson 2000). A previously developed fiber optic SPR sensor used for gas phase dew point determination was modified to liquid-phase sensing by placing a coating of polyethylene glycol (PEG, which has been used in aqueous biphasic extraction for removal of pertechnetate from Hanford and Oak Ridge tank waste) on an SPR system

consisting of a sapphire hemisphere coated with a thin gold film. The SPR sensor generated high-resolution, low-noise SPR spectra suitable for high sensitivity sensing of analyte adsorption onto the sensor surface, and was able to discriminate very small changes in refractive index and show a unique response to 10 ppm perrhenate in NaOH solution.

3.4.3 Summary of Environmental Potential

As a class, spectroscopic techniques (such as PEBBLEs, surface plasmon resonance, or sensing technologies based on nanobelts and nanorods) offer the possibility of detection capabilities down to the single molecule level. Sensing technologies for characterization and monitoring uses are of extreme importance in the environmental field—both for remediation and for process monitoring for pollution prevention applications. The flexibility that can be imparted to nano-enabled sensors means that a wide variety of species can be detected at the lowest levels, and creates a potentially large opportunity for these and similar technologies.

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3.5 Nanowire Sensors

3.5.1 Background

Nanowires are solid, rod-like materials with diameters in the 5-100 nm range, and are most often made from metals or semiconducting metal oxides. Nanowires are different from molecular wires (also sometimes referred to as "molecular nanowires"), which are molecular entities with diameters typically less than 3 nm and repeating subunits. DNA is the premier example of a molecular nanowire, with the repeating subunits being the constituent nucleotides; inorganic examples include $Li_2Mo_6Se_6$ and $Mo_6S_{9-x}I_x$. Research on nanowires is often conducted along with parallel research on carbon nanotubes. Though these materials are different, the sensing mechanisms and underlying behavior are usually very similar. However, it should be noted that there are significant differences in processing and scale-up potential; though similar devices may be made from these nanostructures, this does not mean that similar commercial products will eventually be available.

3.5.2 Description

Nanowire sensors have attracted much attention for two reasons. First, their large surface area to volume ratio promises high sensitivity. Second, the size of the nanostructures is similar to the size of species being sensed, thus the nanostructures make good candidate transducers for producing the signals that are then read and recorded by conventional instruments. The underlying phenomenon exploited in using nanowires is the field effect on which field effect transistors (FETs) are based. The wire acts as the channel from source to drain for the FET. If functional groups attached to the nanowire can act as a receptor to bind with a target species (particularly a biological entity that possesses a charge), then the charge on the surface of the nanowire changes. Since this can influence electronic behavior into the depth of the nanowire, a gating effect occurs that can be used in sensing. Figure 35 provides a representation of a nanowire configured as an FET.

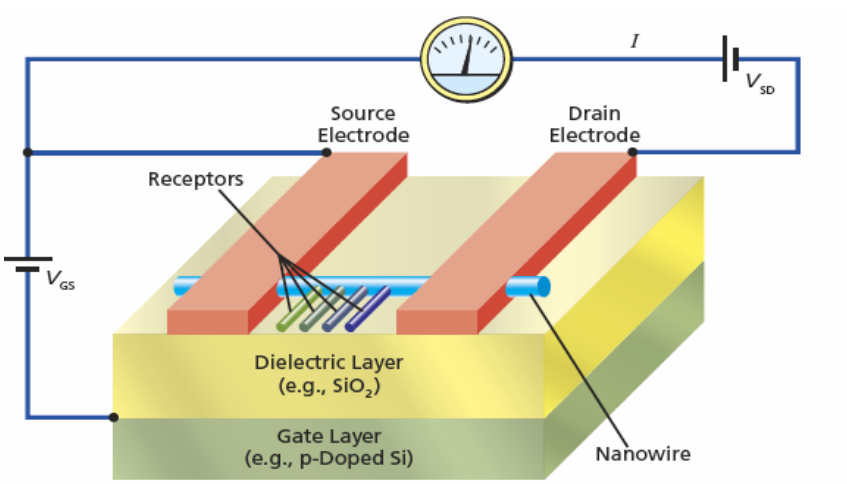

Figure 35. Nanowire in a field effect transistor (FET) configuration

Since they were discovered, silicone nanowires have primarily been investigated for sensing applications in biological systems (Cui et al. 2001). This is because the field effects on a nanowire functionalized with receptors are considerably larger with charged biological species than with ions. Nanowires have been viewed as one of nanotechnology's most promising current products for biomedical research (Hood et al. 2004). Techniques for generating various types of important nanowires, nanorods, nanobelts, and nanotubes, synthetic strategies, research activities unique properties (e.g., thermal, mechanical, electronic, optoelectronic, optical, nonlinear optical, and field emission), and methods for assembling nanostructures into functional devices have been well reviewed (Xia et al. 2003). A comprehensive review of current research activities on chemical sensors based on nanotubes, nanorods, nanobelts, and nanowires, focusing on experimental principle, design of sensing devices, and sensing mechanism has recently been published (Huang and Choi 2007). Other sensing properties of silicon nanowires have been explored, such as gas sensing, where it has been observed that upon exposure to ammonia gas and water vapor, the electrical resistance of the HF-etched relative to non-etched silicon nanowires sample is found to dramatically decrease—even at room temperature (Zhou et al. 2003).

These materials have recently sparked considerable interest in nanoelectronics, in composite nanomaterials, and as conducting polymer nanowire sensors. Sensors and actuators assembled with conductive polymers nanowires are claimed to have superior responding characteristics to their conventional counterparts (Liu et al. 2004, Ramanathan et al. 2004, Alam et al. 2005). Conjugated polymers are organic macromolecules which consist at least of one backbone chain of alternating double and single bonds. This electronic structure allows a pi (π) orbital system, modifiable by intermolecular interactions and other functionalization, to extend along the entire length of the backbone, bestowing one-dimensional conductivity on the polymer. Sensors and sensor arrays based on conjugated polymers and carbon nanotubes have been investigated. The four basic electrical transduction modes—conductometry (monitoring the conductivity changes), potentiometric (monitoring the open circuit potential at zero current), amperometry (monitoring the change in current while the potential is kept constant), and voltammetric (monitoring the change in current while varying the applied potential)—have already been investigated (Dai et al. 2002). Heavy metal-ion sensing for drinking water analysis (Cu^{2+} and Ni^{2+} at parts per trillion range) have been demonstrated using a conducting polymer nanojunction array. Each nanojunction is formed by bridging a pair of nanoelectrodes separated with a small gap with electrodeposited, peptide-modified polyanilines and signal transduction sensing mechanism using the change in conductance due to polymer conformational changes induced by the metal-ion chelating peptide (Aguilar et al. 2005). Dielectrophoretically assembled poly (3,4-ethylenedioxythiophene)/ poly (styrenesulfonate) have been investigated as sensors for acetone, methanol, and ethanol (Dai et al. 2002).

Conducting polymer nanowire sensors have even been formed directly in place in microfluidics devices (Wang et al. 2006). Such an approach has a number of advantages, including:

1. the monomeric precursor polymerizes directly on the electrode surface, producing high-quality ohmic contacts;
2. addressability is inherent to this method because nanowires can be grown across individual electrode junctions;
3. the introduction and delivery of small amounts of precursor monomers and analytes are highly controllable and enable the rapid exchange of nanoliter-level solutions on the same;
4. the turbulence-free environment within a microchannel helps the formation of well-defined conducting polymer nanowires during the electropolymerization process; and
5. once the nanowires are grown, the entire device is ready for use, without the necessity of any postfabrication processing. Figure 36 provides a representation of an actual device.

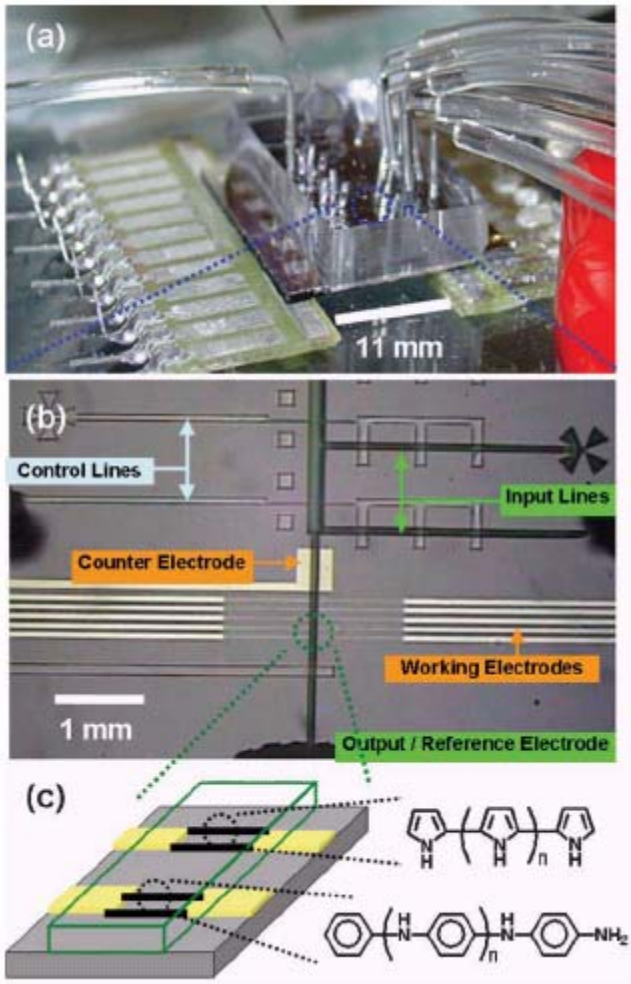

Figure 36. Conducting polymer nanowire sensor formed directly in microfluidics device showing (a) actual view of fabricated device, (b) optical micrograph of microfluidics device and (c) schematic with polyaniline and polypyrrole

Various types of nanowire have been studied for environmental applications other than sensors. For example, natural nanowires in electricigens (microorganisms able to completely oxidize organic compounds to carbon dioxide with the sole electron acceptor being an electrode) (Reguera et al. 2005, Reguera et al. 2006, Reguera et al. 2007); ZVI, iron-nickel, and iron-palladium nanowires have been studied as an alternative to iron nanoparticles in the remediation of chlorinated organics (Yoo et al. 2007); and regenerable gold nanowires have been studied as sensors for mercury (Keebaugh et al. 2007).

3.5.3 Summary of Environmental Potential

Sensors based on nanowires are at an early stage of development. Their large surface area-to-volume ratio promises high sensitivity. Functionalization of the nanowire will allow a variety of species to be sensed.

3.5.4 References

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3.6 Nanobelts and Nanorods

3.6.1 Nanobelts

Nanobelts are a class of nanostructure often viewed as a type of nanowire, usually made from semiconducting metal oxides (such as SnO_2, ZnO, In_2O_3 or CdO, or selenides such as CdSe). Nanobelts form ribbon-like structures with widths of 30-300 nm, thicknesses of 10-30 nm, and lengths in the millimeter range. They are chemically-pure and structurally-uniform single crystals, possessing rectangular cross sections, clean edges, and smooth surfaces.

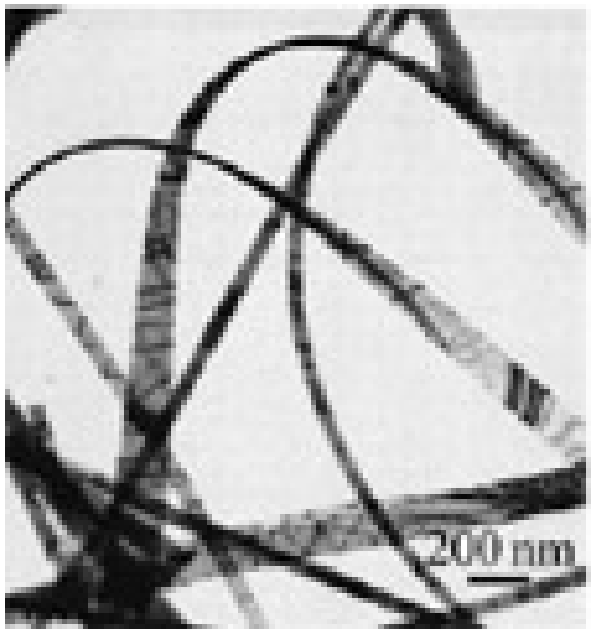

Figure 37. SnO_2 nanobelts

Much research has been conducted on the use of nanobelts as gas sensors. Current gas sensors typically use metal oxides (such as SnO_2) as the sensing element, and operate by measuring changes in electrical conductance of the surface as it undergoes reduction or oxidation reactions with the gas. Though the exact mechanism is not fully understood, it appears that at high temperatures in the absence of oxygen, free electrons move easily through the oxide and across the boundaries between crystal grains. When oxygen is present, it is adsorbed on the oxide surfaces and at the grain boundaries, and (due to its affinity for electrons) it removes free electrons from the underlying material, creating an electron-depleted region and a potential barrier at the grain boundaries. This is manifested as an increase in resistance. In contrast, when a reducing gas is present, it too is adsorbed on the oxide surfaces and at the grain boundaries, where it can react with oxygen, and thus lower the oxygen-generated potential barrier. This is manifested as a reduction in resistance, allowing the sensor to act as a variable resistor dependent on gas concentration.

By virtue of their unique geometry, nanobelts have enormous surface areas per unit mass and most of the material is at the surface. When gases are adsorbed onto the nanobelt surface, the electron depletion or accumulation behavior becomes pronounced (as is the effect on the current flowing along the nanobelt) allowing them to act in a fashion similar to FETs. Further, their small size makes for greatly reduced power consumption over macroscale sensors. Research (Fields et al. 2006, Comini et al. 2002) has shown this behavior to be the basis for effective nanobelt gas sensors, and similar sensors have been made for nerve gas detection (Yu et al. 2005), ethanol sensing (Wan et al. 2004, Xue et al. 2005), and hydrogen sensing (Wang et al. 2005).

Nanobelts possess essentially similar properties to nanowires; they can exhibit FET behavior and have functionalizable surfaces, thus making sensor development strategies for nanowires also available to nanobelts.

3.6.2 Nanorods

Nanorods are solid nanostructures morphologically similar to nanowires but with aspect ratios of approximately 3-to-5. They are formed from a variety of materials including metals, semiconducting oxides, diamonds (aggregated diamond nanorods produced from fullerenes are the hardest material so far discovered), and organic materials. Figure 38 provides an image of ZnO nanorods grown from aqueous solution.

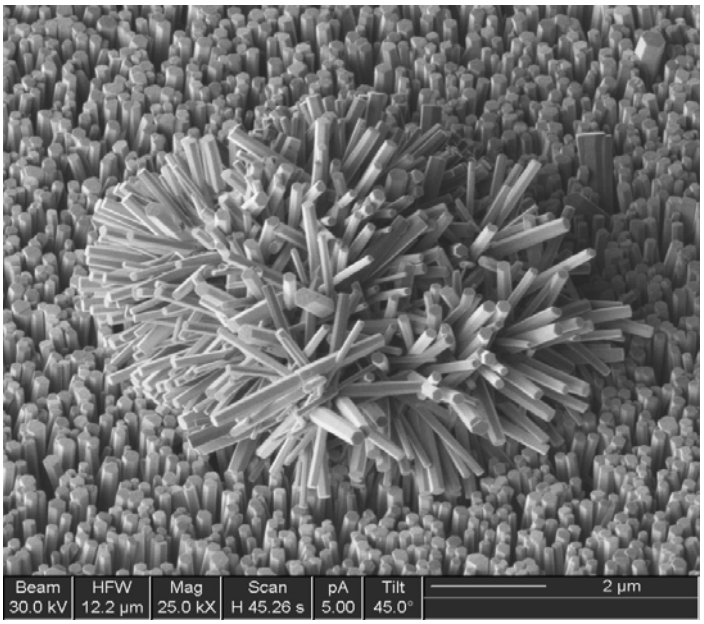

Figure 38. ZnO nanorods grown in aqueous solution

Nanorods are produced by a number of techniques, including: a vapor-liquid-solid approach; mechanical alloying; direct chemical synthesis using ligands for shape control;

plasma arc discharge; laser ablation; and catalytic decomposition (Ayala-Sistos et al. 2005, He et al. 2002, Chopra et al. 1995, Goldberg et al. 1996, Goldberg et al. 2002, Hamilton et al. 1993). They are under considerable investigation for applications such as gas sensors; video displays; computer components; nanoelectronic and nano-optoelectronic components; MEMS devices; and solar energy conversion. One of the factors in their investigation is that both the size and shape can be controlled by use of additives during synthesis so that scaling—as well as basic properties—can be studied (Garcia and Semancik 2007), and flexibility is available for component integration (Benkstein et al. 2006). By functionalizing the nanorods, amphiphilic entities that can self-assemble and form convex curvature can be created—a capability of importance in nanoelectronic and biomedical applications (Park et al. 2004, Chen et al. 2007). Figure 39 provides a graphic representation of a potential structure.

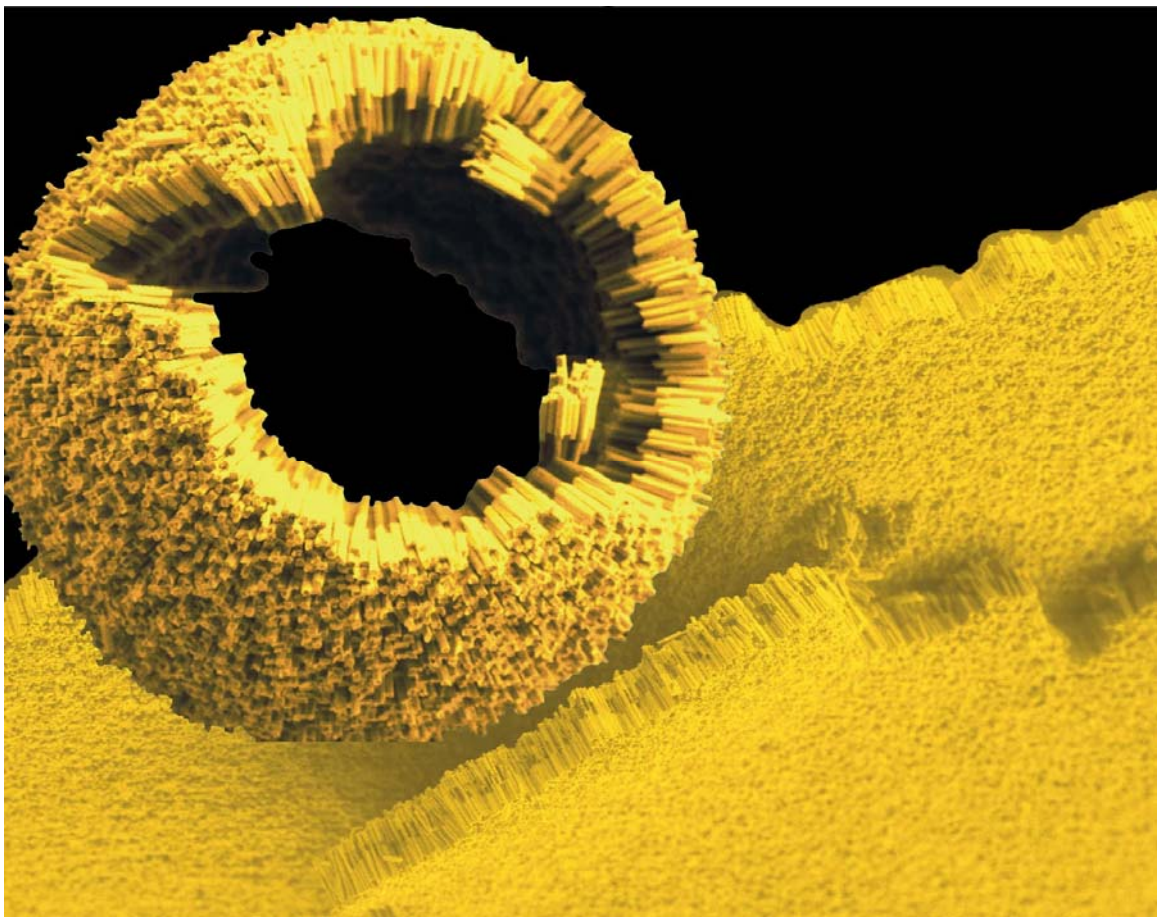

Figure 39. Self-assembly of gold-polymer nanorods into a curved structure

The particular morphology of nanorods also leads to properties that may have unusual, niche applications. For example, the light emitted from or scattered off of gold nanorods is strongly polarized along the rod length axis, an excellent property for an ideal orientation probe (Kou et al. 2006).

Nanorods have recently been subject of a newly demonstrated technique for the fabrication of nanostructures (Zhao et al. 2006). An ideal nanostructure fabrication method would have four desirable features: (1) the ability to control the size, aspect ratio, and shape of the nanostructures; (2) the ability to grow the desired nanostructure at low temperature and onto a particular substrate geometry (e.g., flat, cylindrical, or tapered); (3) the ability to fabricate metallic and dielectric nanostructures with multilayer structures; and (4) the ability to seamlessly integrate the fabrication process with other conventional microfabrication techniques. The following four general approaches have been employed to date:

- nanolithography-based methods which use advanced lithographic techniques, such as electron beam lithography, x-ray lithography, and proximal probe lithography with deposition and plasma etching processes;
- solution-based approaches which use very complicated, controlled wet chemical reactions to synthesize nanostructures and require a detailed understanding of the chemical reaction and crystal growth mechanisms;
- vapor-based methods, such as the vapor-liquid-solid method used since the 1960s, which usually require higher temperatures and a specific catalyst for each structure; and
- template-based methods using host nanoporous materials as forms.

None of these fabrication methods are desirable features of an ideal method of fabricating nanostructured substrates, but Zhao et al. have investigated a novel nanostructure fabrication technique in the production of nanorods called glancing angle deposition (GLAD). GLAD is a physical vapor deposition technique in which the substrate is rotated in the polar and azimuthal directions by two stepper motors programmed by a computer. The experimental results have demonstrated that the GLAD technique offers several strategic advantages compared to other nanofabrication techniques—most particularly that the structures of the nanorods can be well designed by computer programming, a feature that cannot be achieved by any other fabrication technique. Control of this type, by whatever method is important since a novel, tapered form of nanorod, known as "nanorice", has been shown to be the most sensitive surface plasmon resonance nanosensor yet devised (Wang et al. 2006, Srivastava and Lee 2006).

Exploratory work on the use of nanorods for sensors is well underway. A biosensor for determination of heavy metals based on hydrothermally-grown ZnO nanorod/nanotube and metal-binding peptides has been presented. The ZnO acts as an FET and heavy metal binding with a peptide causes an electrical signal change, which can be measured and correlated to the concentration of heavy metals (Jia et al. 2007). A gold nanorod sensor for mercury is able to determine mercury in tap water samples at the parts-per-trillion level has also been developed. The selectivity and sensitivity result from the amalgamation of mercury and gold, and the entire sensing procedure takes less than 10 minutes, with no sample separation and/or sample pre-concentration requirements. The only step prior to mercury determination consists of mixing the water sample with a gold nanorod solution in sodium borohydride. The limit of detection (6.6×10^{-13} $g.L^{-1}$) shows excellent potential for monitoring ultra-low levels of mercury in water samples

(Hernandez et al. 2007). In work on the control of homogeneity in shape, size, and the organization of gold nanorods, the possibility of a copper sensor has been suggested. The basis of the idea is the strong dependence of surface plasmon resonance peaks on the size of gold nanorods, and the detection mechanism is based on the color change due to plasmon-plasmon interaction between adjacent gold nanorods. The gold nanorods were successfully functionalized with glutathione, and the addition of Cu^{2+} ions considerably improves the assembly, opening the possibility of making a copper sensor (Afshar 2007).

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4.0 Observations and Conclusions

This document has synthesized a review of information on existing and potential applications of nano-enabled technologies for remediation and sensing of environmental pollutants, including radionuclides at contaminated sites. Since most environmental nanotechnologies are just emerging and cover a very broad spectrum of potential applications, the approach used in this document is to first present nanotechnologies that are currently being field tested followed by those that are still in the research and/or development stage. A wide range of promising nano-enabled technologies have been presented and discussed to the extent feasible.

It is important to note that the majority of mature (tested and tried) nanotechnologies are dominant in the electronics and biomedical fields. Which nanotechnologies will actually migrate into environmental sensor (and possibly remediation) is challenging to determine at this time with significant accuracy, but comments were made in the document on extrapolation of nanotechnologies across scientific fields where appropriate. In addition to gathering the information presented here, the process of searching and examining the technical literature allowed some broad observations to be made. These collective findings may be summarized as follows:

1. Nano-enabled technologies may be classified into two broad categories: remediation and sensing technologies. Remediation includes detecting, sequestration, and destruction of materials that constitute a threat to pubic health, welfare, and the environment. Sensing technologies, with enhanced sensors using nanomatrials, are used for detecting the presence of pollutants and could be used in monitoring releases for regulatory compliance.

2. The classification in (1) above is most useful in presenting the overall state-of-the-science if: a) a reasonable extrapolation is allowed from related behavior (e.g., it is accepted as reasonable that the success of a technology in the remediation of heavy metals signals the technology's expected success for remediation of radionuclides), and b) the concept of environmental remediation is expanded to include radioactive waste management and radiological decontamination c) sensing of foreign substance or element may also serve as a prerequisite for furthering the development of environmental contaminant detection.

3. In general, our understanding of nanotechnology risk is still developing. More information is needed on both the appropriate framework and on the basic information to be used within that framework. Additionally, the relationship between radionuclides and nanotechnology risk is even more elementary. A growing body of information and knowledge of the fate and transport of various nanomaterials should aid in the assessment of potential risks and mitigation of hazards to public health and the environment posed by nanotechnologies applications.

4. The physical and chemical properties (i.e., high surface area, high reactivity, easy dispersability, rapid diffusion, etc.) of nanomaterials provide the unique properties/capabilities for various environmental nanotech applications. The term "nanomaterial" is very broad and includes nanoparticles (based on overall size or gross dimensions), nanostructured materials (which may be microscale, mesoscale, or even macroscale particles, but still have nanoscale structural features, such as the channels in zeolites), and nanocomposite materials.

5. A number of nano-enabled remediation technologies have either been field tested, trial demonstrated, or are close to and/or awaiting, full-scale implementation. These include ZVI nanoparticles (ZVI microparticles have already been used to remediate uranium contamination of ground water), zeolites (nanostructured materials that have been used in radioactive waste treatment for half a century and have been investigated for the remediation of radioactive cesium in soils, and are now available as nanoparticles), and a radiological decontamination gel (developed at ANL and employing a nanoparticulate radionuclide sorbent). As more nanotechnologies are applied in the field, performance data to include cost, operation and maintenance should be collected real-time to aid in further evaluation, and validating the sustainability of the environmental nanotechnologies applied to radionuclides.

6. Based on analysis of the underlying technical and and scientific framework of a number of available nano-enabled remedial technologies, it is anticipated that nano-enabled technologies will have significant impact in the sensor development area. This is due to well-established fundamentals of sensor behavior that allow distinct advantages to be realized when the sensing events are measured at the molecular level. Despite the great potential for nano-enabled sensors, there are still some major hurdles to overcome in terms of reliable large volume production of nanoscale sensing elements, effective nanoscale manipulation, and integration of the nanoscale sensing elements with the external world.

7. The electronics/biotechnological/biomedical driver for nano-enabled subsystem development has a two-fold benefit. It helps the cause of radionuclide site remediation by maintaining a development impetus, the benefit of which can be taken by those concerned with radionuclides. In doing so, this driver also puts limits on its own utility to radionuclides since biosensing has become the dominant paradigm and many developers are unaware of the needs of the environmental community.

8. The issue of low visibility of environmental needs to the nano-enabled sensing community could easily be addressed by a straightforward communications effort, using avenues such as the Vision 2020 technology partnership or the MATCH Programme in the United Kingdom.

As can be ascertained from this report, nanotechnology is strongly supported by many federal agencies, though relatively little support by comparison is available for environmental applications. In addition, the market for environmental applications is perceived limited in compared to other fields such as biomedical and/or electronics to name a few. This may be a barrier to the rapid development and deployment of nanotechnologies for environmental applications.

As discussed, there are many possible risk concerns associated with nanotechnology. Further, in the case of nanoparticle in situ applications there are risk concerns voiced in the literature and there is no regulatory guidance at this time. Risk concerns are a potential barrier to the acceptance and widespread deployment of nanoparticle based environmental technologies. Further, barriers may include the relatively limited market in environmental nanotechnologies. It seems most likely that nanotechnology-based sensors will be advanced further and will be more widely accepted, with nanotechnologies for remediation developing more gradually.

As explained earlier, the purpose of this document is to provide an overview of the potential applications of nano-enabled technologies and subsystems to radionuclides in the environment, and to further an investigation of case studies to evaluate and validate the sustainability of various applications as they emerge.

Appendix A
Acronyms

AFM	Atomic Force Microscopy
AFO	Amorphous Ferric Oxide
ANL	Argonne National Laboratory
AlPOs	Aluminophosphates
ASTM	American Standard Test Method
CBEN	Center for Biological and Environmental Nanotechnology
DEFRA	Department for Environment, Food, and Rural Affairs
DMRB	Dissimilatory Metal-Reducing Bacteria
DND	Detonation Nanodiamonds
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
DSSR	Double Skin Sheet Reactor
EC	European Commission
EDA	Ethylenediamine
EDF	Environmental Defense Fund
EMSP	Environmental Management Science Program
EPA	U.S. Environmental Protection Agency
EU	European Union
EXAFS	Extended X-Ray Absorption Fine Structure
FDA	Federal Drug Administration
FET	Field Effect Transistor
GLAD	Glancing Angle Deposition
HOPO	Hydroxypyridinone
IAEA	International Atomic Energy Agency
IRGC	International Risk Governance Council
IR	Infrared
ITRC	Interstate Technology & Regulatory Council
ITRS	International Technology Roadmap for Semiconductors
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
LOC	Laboratory-on-a-Chip
LSPR	Localized Surface Plasmon Resonance
MATCH	Multidisciplinary Assessment of Technology Centre for Healthcare
MCDA	multi-criteria decision analysis
MEMS	Microelectromechanical Systems
microTAS	Micro-Total Analytical System
NEAT-ORU	Nanomaterials in the Environment, Agriculture, and Technology Organized Research Unit
NEIC	National Enforcement Investigations Center
NIH	National Institutes of Health
nm	nanometer
NMSP	Nanoscale Materials Stewardship Program
NNI	National Nanotechnology Initiative
NODE	Nanowire-based One-Dimensional Electronics
OAR/OTAQ	Office of Air and Radiation/Office of Transportation and Air Quality
OECA	Office of Enforcement and Compliance Assurance
OPP	Office of Pesticide Programs
OPPT	Office of Pollution Prevention and Toxics
ORD	Office of Research and Development
ORNL	Oak Ridge National Laboratory
OSWER	Office of Solid Waste and Emergency Response

PCB	Polychlorinated Biphenyls
PCE	Perchloroethylene
PEBBLE	Probe Encapsulated By Biologically Localized Embedding
PEG	Polyethylene Glycol
PNNL	Pacific Northwest National Laboratories
PRB	Permeable Reactive Barrier
R&D	Research and Development
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-Trinitro-Triazine
RO	Reverse Osmosis
RS/RAE	Royal Society/Royal Academy of Engineering
SAMMS	Self-Assembled Monolayers on Mesoporous Supports
SBIR	Small Business Innovation Research
SCENIHR	Scientific Committee on Emerging and Newly Identified Health Risks
SES	Steward Environmental Solutions
SETAC	Society of Environmental Toxicology and Chemistry
SPR	Surface Plasmon Resonance
STAR	Science To Achieve Results
STM	Scanning Tunneling Microscope
SWCNT	Single-Walled Carbon Nanotubes
TCA	Trichloroethane
TCE	Trichloroethylene
TDS	Total Dissolved Solids
TNT	2,4,6-Trinitrotoluene
UNCD	Ultrananocrystalline diamonds
USNRC	U.S. Nuclear Regulatory Commission
VOC	Volatile Organic Compound
WSCP	Water-Soluble Chelating Polymers
ZVI	Zero-Valent Iron

Appendix B
Glossary

Array: An arrangement of sensing elements in repeating or non-repeating units that are arranged for increased sensitivity or selectivity.

Assembler: A general-purpose device for molecular manufacturing capable of guiding chemical reactions by positioning molecules.

Atomic force microscope (AFM): An instrument able to image surfaces to molecular accuracy by mechanically probing their surface contours. A kind of proximal probe.

Buckyball/C-60: see **Fullerenes**, of which "buckyballs" is a subset. The term "buckyball" refers only to the spherical fullerenes and is derived from the word "Buckminsterfullerene," which is a geodesic dome/soccer ball-shaped C-60 molecule. C-60 was the first buckyball to be discovered and remains the most common and easy to produce.

Cantilever: A beam supported at one end and capable of defined bending and vibrational behavior.

Catalyst: A substance, usually used in small amounts relative to the reactants, that modifies and increases the rate of a reaction without being consumed or changed in the process.

Chemical Sensor: A device capable of providing quantitative or semi-quantitative information on a chemical species (or analyte) through calibration, and then brought into direct contact with the species in its environment.

Conjugated Polymers: Organic macromolecules that consist at least of one backbone chain of alternating double and single bonds.

Dendrimers: Artificially-engineered or manufactured molecules built up from branched unites called monomers. Technically, a dendrimer is a branched polymer, which is a large molecule comprised of many smaller ones linked together.

Depth Filters: A type of filter in which the filter medium has a significant physical depth and the particles to be retained are captured throughout the depth of the filter.

Disruptive Technology: Introduced in 2003, this term is used to describe a new technology that is significantly cheaper (or performs better) than a current technology.

Electron beam lithography: Lithographic patterning using an electron beam, usually to induce a change in solubility in polymer films. The resulting patterns can be subsequently transferred to other metallic, semiconductor, or insulating films.

Electrospinning: A process for making nanofibers with diameters down to about 10 nm using an electrical charge to elongate and narrow fibers formed by an added melt.

Enabling science and technologies: Areas of research relevant to a particular goal, such as nanotechnology.

Engineered/manufactured nanomaterials: Nanosized materials that are purposefully made. These are in contrast to incidental and naturally-occurring nanosized materials. Engineering/manufacturing may be done through certain chemical and/or physical processes to create materials with specific properties. There are both "bottom-up" processes (such as self-assembly) that create nanoscale materials from atoms and molecules, as well as "top-down" processes (such as milling) that create nanoscale materials from their macro-scale counterparts. Nanoscale materials that have macro-scale counterparts frequently display different or enhanced properties compared to the macro-scale form.

Exploratory engineering: Design and analysis of systems that are theoretically possible but cannot be built yet, owing to limitations in available tools.

Exposure assessment: The determination or estimation (qualitative or quantitative) of the magnitude, frequency, duration, route, and extent (number of people) of exposure to a chemical, material, or microorganism.

Fullerenes: Pure carbon, cage-like molecules composed of at least 20 atoms of carbon. The word "fullerene" is derived from the word “Buckminsterfullerene,” which refers specifically to the C-60 molecule and is named after Buckminster Fuller, an architect who described and made famous the geodesic dome. C-60 and C-70 are the most common and easy to produce fullerenes.

Green Rust: A class of Iron II/Iron III hydroxide compounds having a pyroaurite-type structure consisting of alternating positively charged hydroxide layers and hydrated anion layers.

Incidental nanosized materials: Nanomaterials that are the byproducts of human activity, such as combustion, welding, or grinding.

Lab-on-a-Chip (LOC): Also known as a micro-total-analytical system (microTAS), or microfluidics device, is a device that can integrate miniaturized laboratory functions, such as separation and analysis of components of a mixture, on a single microprocessor chip using extremely small fluid volumes on the order of nanoliters to picoliters.

Limited assembler: Assembler capable of making only certain products; faster, more efficient, and less liable to abuse than a general-purpose assembler.

Macroporous: Mesoporous materials with a pore diameter range greater than 50 nm.

Membrane filter: A filter that uses relatively thin material with a well-defined maximum pore size, with particle retaining effects taking place almost entirely at the surface.

Mesoporous materials: Porous substances with pore diameters in the range of 2-50 nm.

Microcantilever: A very small cantilever, the properties of which can be understood from basic engineering principles.

Microfluidics: An interdisciplinary field dealing with the behavior and control of extremely small volumes of fluids and the design of systems that use these small volumes.

Microporous: Mesoporous materials with a pore diameter range less than 2 nm.

Molecular manufacturing: Manufacturing using molecular machinery, giving molecule-by-molecule control of products and by-products via positional chemical synthesis.

Molecular nanotechnology: Thorough, inexpensive control of the structure of matter based on molecule-by-molecule control of products and byproducts; the products and processes of molecular manufacturing, including molecular machinery.

Molecular recognition: A chemical term referring to processes in which molecules adhere in a highly specific way, forming a larger structure; an enabling technology for nanotechnology.

Nano-: A prefix meaning one billionth (1/1,000,000,000).

Nanobelts: A class of nanostructure often viewed as a type of nanowire, usually made from semiconducting metal oxides, such as SnO2, ZnO, In_2O_3 or CdO, or selenides such as CdSe. Nanobelts form ribbon-like structures with widths of 30-300 nm, thicknesses of 10-30 nm, and lengths in the millimeter range.

Nanoelectronics: Electronics on a nanometer scale, whether by current techniques or nanotechnology; includes both molecular electronic and nanoscale devices resembling today's semiconductor devices.

Nanomanufacturing: Same as molecular manufacturing.

Nanometer: One billionth of a meter.

Nanoparticle: Free standing nanosized material, consisting of between tens to thousands of atoms.

Nanorods: Solid nanostructures morphologically similar to nanowires but with aspect ratios of about 3-to-5. They are formed from a variety of materials including metals,

semiconducting oxides, diamonds (aggregated diamond nanorods produced from fullerenes are the hardest material so far discovered), and organic materials.

Nanoscale: Having dimensions measured in nanometers.

Nanoscience: The interdisciplinary field of science devoted to the advancement of nanotechnology.

Nanosensors: Chemical sensors possessing a nanoscale sensing element.

Nanostructures: Structures at the nanoscale; that is, structures of an intermediate size between molecular and microscopic (micrometer-sized) structures.

Nanotechnology: Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1-100 nm range; creating and using structures, devices, and systems that have novel properties and functions because of their small and/or intermediate size; and the ability to control or manipulate on the atomic scale.

Nanotube: Tubular structure, carbon and non-carbon based, with dimensions in the nanometer regime.

Nanowire: High aspect ratio structures with nanometer diameters that can be filled (nanorods) or hollow (nanotubes).

PEBBLE (Probe Encapsulated by Biologically Localized Embedding): sub-micron sized optical sensors designed specifically for minimally invasive analyte monitoring in viable, single cells.

Point-of-Care: Analytical testing performed outside the central pathology laboratory using a device or devices that can be easily transported to the vicinity of the patient.

Quantum dot: A closely packed semiconductor crystal comprised of hundreds or thousands of atoms, and whose size is on the order of a few nanometers to a few hundred nanometers. Changing the size of quantum dots changes their optical properties.

Scanning Tunneling Microscope (STM): An instrument able to image conducting surfaces to atomic accuracy; has been used to pin molecules to a surface.

Sealed assembler lab: A general-purpose assembler system in a container permitting only energy and information to be exchanged with the environment.

Self-Assembled Monolayers on Mesoporous Supports (SAMMS): Nanoporous ceramic materials that have been developed to remove contaminants from environmental media.

Self-assembly: The ability of objects to assemble themselves into an orderly structure. Routinely seen in living cells, this is a property that nanotechnology may extend to inanimate matter.

Self-replication: The ability of an entity such as a living cell to make a copy of itself.

Spectroscopy: The scientific study of the absorption, emission, or scattering of electromagnetic radiation by atoms, molecules, ions, solids, liquids, or gases.

Sticking Coefficient: A standard term in surface chemistry and surface physics. It is the ratio of the number of adsorbate molecules that adsorb, or "stick", to a surface, to the total number of molecules that impinge upon that surface during the same period of time. A value of 1.00 means all impinging molecules stick, while a value of 0.00 means none stick. The concept is used in investigations of nanoparticle mobility in the subsurface.

Superlattice: Nanomaterials composed of thin crystal layers. The properties (thickness, composition) of these layers repeat periodically.

Surface Modified Membranes: Using technology to change the surface of the membrane, but not the underlying bulk material.

Water-Soluble Chelating Polymers (WSCP): Polymers engineered to contain both highly elective chelating functionalities to bind with targeted metal ions, and solubilizing functionalities to allow the polymer to dissolve in water.

Zeolite: A mineral with a pore size of less than 1 nm.

Appendix C
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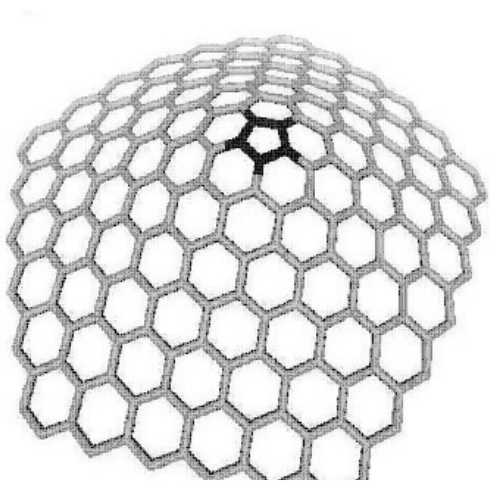

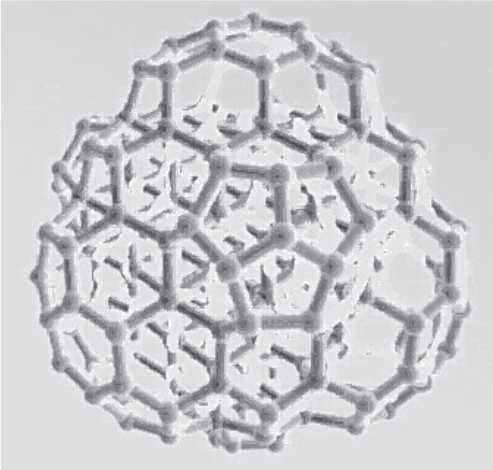

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